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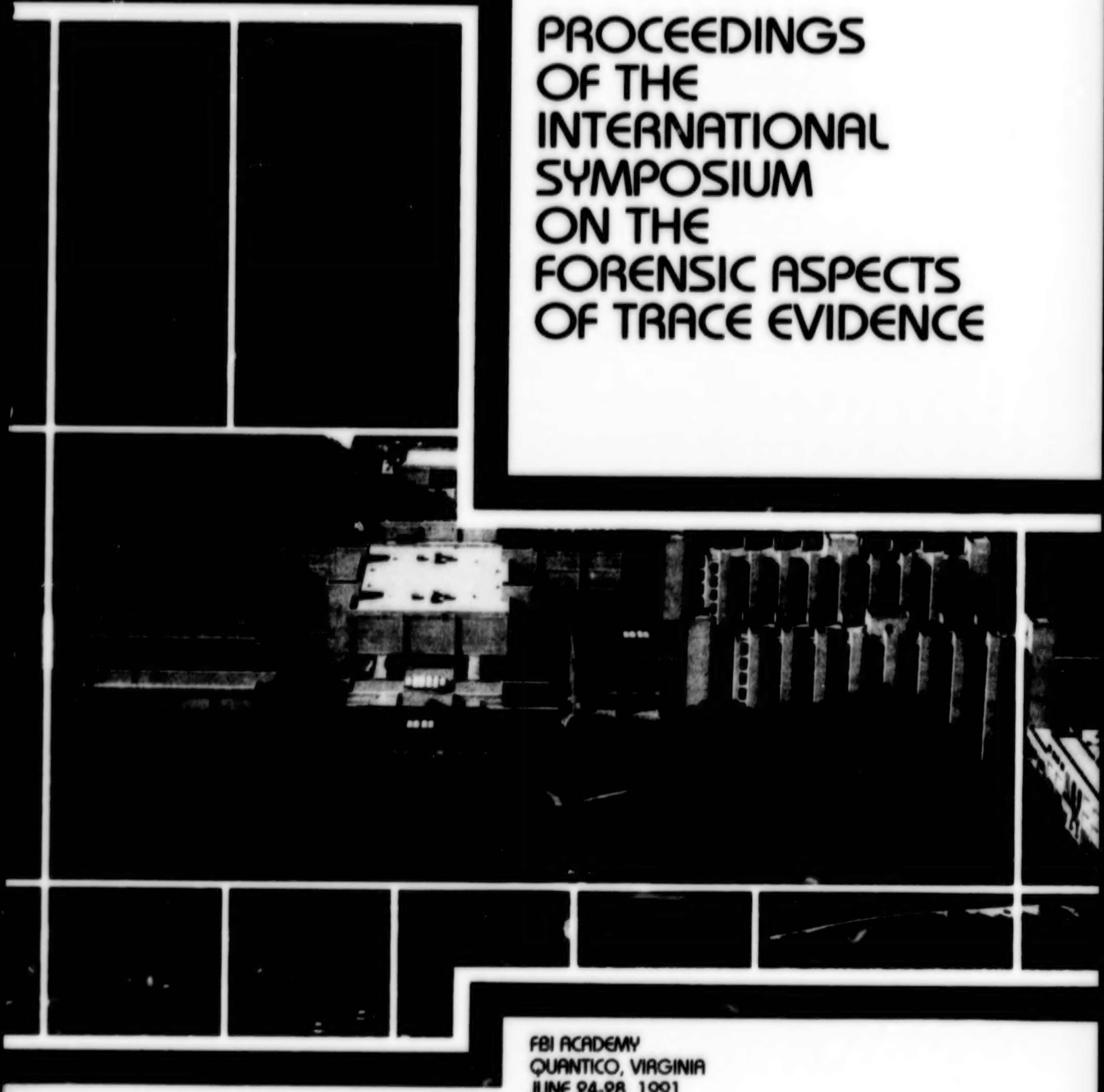

PROCEEDINGS OF THE INTERNATIONAL SYMPOSIUM ON THE FORENSIC ASPECTS OF TRACE EVIDENCE

FBI ACADEMY
QUANTICO, VIRGINIA
JUNE 24-28, 1991

Proceedings of the International Symposium on the Forensic Aspects of Trace Evidence

Host
Laboratory Division
Federal Bureau of Investigation

June 24–28, 1991

Forensic Science Research and Training Center

FBI Academy

Quantico, Virginia

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FOREWORD

On June 24-28, 1991, the FBI Laboratory Division hosted an "International Symposium on the Forensic Aspects of Trace Evidence" at the FBI Laboratory's Forensic Science Research and Training Center, FBI Academy, Quantico, Virginia. This symposium was attended by over 200 scientists from industry, academia and crime laboratories from throughout the United States, Belgium, Canada, Great Britain, Israel, Italy and Japan.

We in the forensic science community recognize that violent crime continues to plague the cities and towns in our respective countries. It is the crime laboratory that is generally the recipient of the voluminous amount of physical evidence related to these crimes and charged with the responsibility to scientifically determine its evidentiary value. In past years we have attempted to focus our symposia topics on specific forensic disciplines such as DNA, hairs and fibers, questioned documents and latent prints. After conferring with the crime laboratory community, it was decided to host a symposium on the general topic of trace evidence, excluding the area of hair and fiber type evidence.

After the topic was selected, we assembled a panel of individuals from the FBI Laboratory representing the many diverse fields to assist in planning the program and identifying the plenary speakers. In addition, Dr. Ralph Allen from the University of Virginia assisted during these planning stages. The program committee reviewed over 50 excellent abstracts from individuals wishing to present posters. Unfortunately only a portion of these could be accepted due to space limitations at the poster sessions.

We sincerely hope that the exchange of information and ideas at this symposium will assist in the examination of trace evidence and generate interest into future research in this. We in the FBI Laboratory will continue to sponsor symposia in various scientific disciplines with the dedicated purpose of providing a forum for the transfer of information and technology. On behalf of the FBI Laboratory, we would like to thank all those who participated in making this symposium a success.

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SECTION I

LECTURES

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IS IT JUST GRIME OR A CRIME: THE REAL DIRT ON THE LEGAL ASPECTS OF TRACE EVIDENCE

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THE LEGAL VALUE OF TRACE EVIDENCE

Direct vs. Circumstantial Evidence

Black's Law Dictionary 460 (6th ed. 1990) defines direct evidence as "Evidence in form of testimony from a witness who actually saw, heard or touched the subject of questioning. Evidence which, if believed, proves existence of fact in issue without inference or presumption." An example of direct evidence would be testimony from an eyewitness to a crime.

Black's Law Dictionary at 243 defines circumstantial evidence as "Testimony not based on actual personal knowledge or observation of the facts in controversy, but of other facts from which deductions are drawn, showing indirectly the facts sought to be proved." An example of circumstantial evidence would be the testimony from the forensic scientists in the woodchipper murder case in Connecticut. A husband was charged with murdering and grinding up his wife in a woodchipper. The only evidence which remained consisted of bone fragments, hair and a tooth.

Thus, trace evidence is usually circumstantial evidence. The law states that direct evidence and circumstantial evidence are both given equal weight. In many jurisdictions the court instructs the jury that both types of evidence are sufficient to prove the elements of a crime. See, for example, the following standard jury instructions for federal criminal cases:

Definition of Direct and Circumstantial Evidence

> There are two types of evidence: direct and circumstantial. Direct evidence is the testimony of a person who claims to have personal knowledge of the commission of the crime which has been charged, such as an eyewitness. Circumstantial evidence is the proof of a chain of facts and circumstances which tend to show whether the defendant is guilty or not guilty. The law makes no distinction between the weight to be given either direct or circumstantial evidence. Therefore, all of the evidence in the case, including the circumstantial evidence, should be considered by you in arriving at your verdict.

Instruction 3.02, Federal Criminal Jury Instructions, Seventh Circuit (1990).

Evidence - Inferences - Direct and Circumstantial

> So, while you should consider only the evidence in the case, you are permitted to draw such reasonable inferences from the testimony and exhibits as you feel are justified in the light of common experience. In other words, you may make deductions and reach conclusions which reason and common sense lead you to draw from the facts which have been established by the testimony and evidence in the case.
>
> You may also consider either direct or circumstantial evidence. "Direct evidence" is the testimony of one who asserts actual knowledge of a fact, such as an eye witness. "Circumstantial evidence" is proof of a chain of facts and circumstances indicating either the guilt or innocence of the Defendant. The law makes no distinction between the weight to be given to either direct or circumstantial evidence. It requires only that you weigh all of the evidence and be convinced of the Defendant's guilt beyond a reasonable doubt before he can be convicted.

Instruction 5, Pattern Jury Instructions, Criminal Cases, Fifth Circuit (1990).

The law requires that the *corpus delicti*, the body of the crime or the body of evidence must be proven in all cases. Trace evidence is very useful in proving the corpus delicti.

A recent New York case, *People* v. *Metro*, 569 N.Y.S.2d 673 (N.Y.A.D. 1991), which concerned a hit and run illustrates the importance of trace evidence. The defendant killed two people and a dog. The court held that the circumstantial evidence, paint chips in the victim's clothing, and animal hair on the car, was sufficient to uphold a conviction for criminally negligent homicide.

Admissibility of Trace Evidence

Two different tests for admissibility of scientific evidence are used by courts in the United States today. The majority of states still use the *Frye* test. *Frye* v. *United States*, 293 F. 1013 (D.C. Cir. 1923). The *Frye* "general acceptance" test for admissibility of novel scientific evidence is drawn from the oft-quoted language of the case:

> Just when a scientific principle or discovery crosses the line between the experimental and demonstrable stages is difficult to define. Somewhere in this twilight zone the evidential force of the principle must be recognized, and while courts will go a long way in admitting expert testimony deduced from a well-recognized scientific principle or discovery, the thing from which the deduction is made must be sufficiently established to have gained general acceptance in the particular field in which it belongs. *Id.* at 1014.

A second test for the admissibility of scientific evidence follows the test set forth in Federal Rule of Evidence 702:

> If scientific, technical, or other specialized knowledge will assist the trier of fact to understand the evidence or to determine a fact in issue, a witness qualified as an expert by knowledge, skill, experience, training, or education, may testify thereto in the form of an opinion or otherwise.

Therefore, pursuant to Rule 702 the court will ask whether the evidence is reliable and whether it will assist the trier of fact. But the court also determines whether such evidence is too prejudicial. This requirement is set forth in Federal Rule of Evidence 403 which states:

> Although relevant, evidence may be excluded if its probative value is substantially outweighed by the danger of unfair prejudice, confusion of the issues, or misleading the jury, or by considerations of undue delay, waste of time, or needless presentation of cumulative evidence.

A recent Florida case illustrates this point. In *State* v. *Sawyer*, 561 So. 2d 278 (Fla. 2d Dist. Ct. App. 1990), the court held that hair evidence was inadmissible where the evidence could have seriously prejudiced the defendant. In this case the trial court granted the defendant's motion *in limine* to exclude hair as evidence in a first degree murder case. The victim was discovered beaten, tortured and murdered in her apartment. During the course of the investigation several unknown hairs were found on or around the victim's body in her upstairs bedroom, and one unknown hair was found beneath the kitchen window. During the motion hearing, an expert in microanalysis testified the one unknown pubic hair found under the kitchen window had not been forcibly removed and did not match the other unknown hairs found in the victim's apartment. *Sawyer*, at 283. The hair matched Sawyer's pubic hair sample in twenty observable characteristics. Id. The expert testified that this did not mean the hair was absolutely identified as belonging to Sawyer but rather the hair came from someone within a class of individuals having the same hair characteristics as the defendant. *Id.*

The expert also testified that the hair could have been transferred by other means. Numerous people walked in and out of the crime scene during the time evidence was being collected and may have contaminated the scene. The agent could not testify as to how a given hair could get to a particular location, especially in light of the extensive contamination. Because the hair could not be positively identified as being from Sawyer and was not probative in proving that Sawyer was in the victim's apartment at the time of the murder, the appellate court held that the trial judge properly ruled the evidence to be inadmissible. *Id.* at 284.

Contrast the holding in *Sawyer* with a recent North Carolina case, *State* v. *Dar*, 397 S.E. 2d 634 (N.C. App. 1990). In *Dar* a North Carolina trial court admitted hair and fiber evidence taken from defendant's pants notwithstanding his claim that he could have picked up the evidence by riding in the back seat of the police car in which the victim had ridden earlier that day. The appellate court held that his argument went to the weight of the evidence, not to its admissibility, and upheld the trial court's decision to admit the hair and fiber evidence.

A trial court judge's decision regarding the admissibility of such evidence will only be overturned if the appellate court determines he abused his discretion. For example, in *State* v. *Williams*, 400 S.E. 2d 131 (S.C. 1991), the Court held it was an abuse of discretion to admit testimony and evidence concerning racial types from whom hair samples found on a blanket seized from bedroom closet in defendant's home would have come. The blanket containing the analyzed hair was seized approximately 19 months after victim's disappearance. The expert testified that his analysis merely narrowed identification to categories of persons. The court held the evidence inadmissible in that it was obtained at a time too remote from the victim's disappearance and lacked sufficient connection to the victim to constitute relevant proof. Therefore the appellant was unfairly prejudiced.

In *N.C.* v. *Faircloth*, 394 S.E. 2d 198 (N.C. App. 1990), a rape case, the expert stated it was impossible that hairs could have originated with someone other than defendant. However, this improper testimony concerning conclusions to be drawn from hair analysis was not reversed since the defense did not move to strike the expert's responses to questions during trial. Thus, the defense did not preserve the issue for appeal.

Weight Accorded Trace Evidence

Once a court admits scientific evidence (a question of law), the jury as fact-finder must determine the weight to give it. In most jurisdictions the judge instructs the jury that direct or circumstantial evidence may be used to prove the elements of a case.

Scientific evidence is very compelling. National Institute of Justice studies have shown that jurors are persuaded by such evidence (Peterson *et al.* 1984, 1986). Sentences tend to be more severe when forensic evidence is presented at trials. Id.

Illsely (1987) provides a valuable resource for gaining insight into jurors' perceptions of expert testimony. The study examined 1500 jurors' perceptions of fingerprint experts, but it's findings are useful to all experts. Some highlights:

1 — Jurors find experts' qualifications very persuasive;

2 — Jurors find training and experience to be the most important qualifications (more so than degrees); and

3 — A majority of jurors felt that the experts who belonged to professional associations or groups were more persuasive and credible, the "better" experts.

Note that even though the evidence is persuasive the expert must be both persuasive and credible. Jurors are instructed by the court that they may evaluate an expert's testimony in the same manner as a lay witness's testimony. For example, in Florida the court instructs the jury as follows:

> **2.04(a) Expert Witnesses**
>
> Expert witnesses are like other witnesses, with one exception -- the law permits an expert witness to give his opinion.
>
> However, an expert's opinion is only reliable when given on a subject about which you believe him to be an expert.
>
> Like other witnesses, you may believe or disbelieve all or any part of an expert's testimony.

LEGAL OBSTACLES

Failure to Obtain Trace Evidence

There is increased public awareness of the availability and value of scientific evidence, especially trace evidence. Media exposure - papers, TV, even the movies - like Presumed Innocent and Silence of the Lambs expose the public to scientific evidence. While public awareness of the value of forensic evidence is desirable, it also leads to certain expectations. Jurors now expect scientific evidence. If none is presented at trial they ask "Where are the fingerprints, hairs, fibers, soil or paint chips?" So an expert may now be called to testify why no trace evidence was present - or worse - why none was obtained due to unprofessional crime scene work. The following scenario provides an illustration. A person was found in a car in a canal. Instead of first carefully searching the scene for trace evidence, the police department flew in its new helicopter to lift the car out, thus destroying all trace evidence. That's the type of case in which an expert may be called to explain why no trace evidence was found.

Illegal Search and Seizure of Trace Evidence

If evidence was improperly seized the prosecution may be precluded from using it at trial, no matter what your analysis reveals. How does this effect the expert? You may have information regarding the seizure of the evidence that is valuable to the prosecutor. The seizing officer may provide you with more background information than the prosecutor. This additional information may aid the prosecutor in defending a motion to suppress the seized evidence. The prosecution is legally obligated to reveal exculpatory evidence to the defense and some of the information you have regarding the evidence may fall in that category, thus you must inform the prosecution.

Here are brief synopses of the three most recent U.S. Supreme Court cases on search and seizure:

In *Florida* v. *Jimeno*, 111 S.Ct. 1801 (1991), the defendant was stopped for a traffic violation after police overheard him engaging in a drug deal. Jimeno consented to a car search. Police found the drugs in a paper bag hidden under the floor board. The Court held it was not an unreasonable search since he gave permission to search the car. Therefore it is permissible for the police to open any closed containers that might reasonably hold the object of the search.

In *California* v. *Acevedo*, 111 S.Ct. 1982 (1991), the DEA and California Police Department, working together, seized a package containing drugs and sent it on to the recipient at Federal Express. Some officers left for a search warrant for the recipient's home while others waited. A person arrived and left with a blue knapsack. The police searched it and found marijuana. Acevedo left the house with a bag. The officers observed him put it in the car trunk. They followed him and pulled him over in a marked car and searched the trunk and bag. All this activity occurred within two hours.

The defense moved to suppress the evidence. The Court held that the police may search a container located in an auto and need not hold the container until they obtain a warrant even though they lack probable cause to search the vehicle as a whole, as long as they have probable cause to search the container.

Florida v. *Bostick*, 111 S.Ct. 2382 (1991), concerned consent searches on buses. The U.S. Supreme Court said the Florida Supreme Court erred in adopting a *per se* rule that every encounter on a bus is a seizure. The appropriate test, according to the Court, is whether, taking into account all the circumstances surrounding the encounter, a reasonable passenger would feel free to decline the officers' request or terminate the encounter. A consensual encounter does not trigger Fourth Amendment scrutiny even when the officers have no basis for suspecting a particular individual. They may ask a person questions provided they do not convey a message that compliance with their request is required. The case was remanded.

Chain of Custody

Tangible evidence of a crime is admissible when it is shown to be in substantially the same condition as when the crime was committed. It is presumed that the integrity of evidence routinely handled by governmental officials is suitably preserved unless the defendant makes a showing of bad faith, evil motivation, or some evidence of tampering. If the defense makes such a showing, the Government must establish that acceptable precautions were taken to maintain the evidence in its original state. Then the prosecutor must show the evidence was handled according to established procedures.

If an expert witness is going to testify about the scientific analysis of a piece of evidence, the predicate must include proof of the chain of custody of the evidence from the time of initial seizure to the time of final analysis. The chain of custody witnesses set the stage for the testimony by the expert witnesses.

A complete foundation for scientific testimony includes four parts: (1) proving the chain of custody for any physical sample between the time of seizure and the time of analysis; (2) teaching the trier of fact about the scientific theory and instrument; (3) describing the specific occasion when the instrument was used to analyze the sample; and (4) interpreting the test result for the trier of fact. Imwinkelried, The Methods of Attacking Scientific Evidence 82 (1982). In some cases, the lawyer will call four different witnesses to lay the various parts of the foundation. However, one witness could testify to all four elements of the foundation.

Proof of the chain of custody is necessary if an object is not unique or if the seizing person failed to note a unique trait at the time of seizure or can no longer remember the trait. The chain of custody also needs to be proven in cases in which the evidence's condition, not just mere identity, must be proven, for example, when a pair of underwear is recovered from a rape victim, but it has stains and hairs on it. If the attorney wants to introduce the scientific analysis of the stains and hairs that place in issue the object's condition at the time of analysis a chain of custody is necessary. See *Robinson* v. *Commonwealth*, 212 Va. 136, 183 S.E.2d 179 (1971).

A person does not become a link in the chain of evidence by virtue of mere access to the evidence. A person becomes a link only if the person physically handles the object. So if 20 people work in a lab with access to the evidence, only those who actually handle it are in the chain.

There is no requirement that every person qualifying as a link need testify at trial. For example, the agent testifies that he delivered a sample to a secretary at the laboratory, and the laboratory technician adds that he received the labelled sample from the secretary with the seal unbroken. Must the secretary testify? Courts have sustained the chain in similar cases. See *United States* v. *Picard*, 464 F.2d 215 (1st Cir. 1972). The courts reason that proof of the label and seal creates an inference that the secretary neither substituted for, nor tampered with the sample. Imwinkelried, "The Identification of Original, Real Evidence," 61 Mil. L. Rev. 145, 159-60 (1973).

Courts demand some showing of safeguarding by each link in the chain. Laboratories' chain-of-custody receipts would be admissible as substantive proof. If the receipt lists a handler the proponent has not accounted for, the receipt establishes an obvious break in the chain. Lawyers are suspicious if the chain seems to leap straight from the person who initially collected the sample to the laboratory analyst who ran the test. They know, in most cases, there is an intermediary; the collector may have delivered the sample to a receptionist, secretary, or mail clerk who, in turn, delivered the sample to the analyst in the testing area. A court may evaluate the proof of a chain of custody much more rigorously when the evidence is fragile as is the case with trace evidence.

Discovery

The criminal rules of procedure, for example, Federal Rule Criminal Procedure 16, put certain obligations on the prosecutor and defense regarding discovery. The expert is also effected since she must provide the required information to the state, who will turn it over to the defense. For example, if you don't tell the prosecutor about certain evidence that he must disclose, the government will be sanctioned. Sanctions for failing to comply with discovery range from contempt to mistrial. Sanctions against prosecution or defense may involve prohibiting a party from introducing at trial evidence not disclosed through the discovery process.

Particular discovery obligations which effect the government expert are found in Federal Rule of Criminal Procedure 16(a)(1)(D):

> Upon request of a defendant the government shall permit the defendant to inspect and copy or photograph any results or reports of physical or mental examinations, and of scientific tests or experiments, or copies thereof, which are within the possession, custody, or control of the government, the existence of which is known, or by the exercise of due diligence may become known, to the attorney for the government, and which are material to the preparation of the defense or are intended for use by the government as evidence in chief at the trial.

The expert's report clearly falls in that category. The defense has a reciprocal obligation as well. Federal Rule of Criminal Procedure 16(b)(1)(B) provides:

> If the defendant requests disclosure under subdivision (a)(1)(C) or (D) of this rule, upon compliance with such request by the government, the defendant, on request of the government, shall permit the government to inspect and copy or photograph any results or reports of physical or mental examinations and of scientific tests or experiments made in connection with the particular case, or copies thereof, within the possession or control of the defendant, which the defendant intends to introduce as evidence in chief at the trial or which were prepared by a witness whom the defendant intends to call at the trial when the results or reports relate to that witness' testimony.
>
> It is a continuing duty.

The United States Supreme Court case of *Brady* v. *Maryland*, 373 U.S. 83 (1963), requires the government in criminal cases to provide the defense with all exculpatory information, that is, evidence that is material to either the guilt or punishment of the defendant. So if your findings show that the decedent was the aggressor in the fight, for example, fingernail scrapings of defendant show trace evidence consistent with the defense theory of self defense -- the prosecutor must provide that information to the defense.

Destruction of Trace Evidence

The defense may allege that a defendant's due process rights were violated because the expert did not preserve the evidence or the expert used it all in testing. The leading case addressing this situation is *Arizona* v. *Youngblood*, 488 U.S. 51 (1988).

The victim, a 10-year-old boy, was molested and sodomized by a middle-aged man for 1 1/2 hours. After the assault, the boy was taken to a hospital where a physician used a swab from a "sexual assault kit" to collect semen samples from the boy's rectum. The police collected the boy's clothing, which they failed to refrigerate. A police criminalist later performed some tests on the rectal swab and the boy's clothing, but he was unable to obtain information about the identity of the boy's assailant. At trial, expert witnesses testified that the respondent might have been completely exonerated by timely performance of tests on properly preserved semen samples.

The U. S. Supreme Court held that the Due Process Clause of the U. S. Constitution did not require the State to preserve the semen samples even though the samples might have been useful to the respondent. Unless a criminal defendant can show bad faith on the part of the police, failure to preserve potentially useful evidence does not constitute a denial of due process of law. Here, the police's failure to refrigerate the victim's clothing and to perform tests on the semen samples can at worst be described as negligent. Negligence is not bad faith.

A recent New York trial court case held that if a sample is still preserved after trial the defendant has a right to test it with new scientific methods, for example, a DNA test, even after his conviction. In *Dabbs* v. *Vergari*, 570 N.Y.S.2d 765 (Sup. Ct. Westchester Co. 1990), semen stained clothes from a 1984 rape trial were still preserved and the Court held the defendant had a right to test them.

If there is intentional destruction of evidence, there is not only a due process argument, but also a crime of obstruction of justice. Thirty-six states and the District of Columbia have statutes that specifically prohibit the destruction of evidence. It may also be contempt if you destroy evidence subpoenaed by a grand jury or court.

Cross-Examination

There are basically four purposes of cross-examination:

1 — To discredit the witness;

2 — To elicit testimony from the witness which discredits unfavorable testimony given by other witnesses on the same side -- creating a conflict with testimony of other witnesses on the same side;

3 — To elicit testimony to corroborate favorable testimony;

4 — To elicit testimony to contribute independently to the theory of your case.

Entire books have been written on cross-examination. See, for example, W. Mulligan, Expert Witnesses: Direct and Cross-Examination (1987); R. Aron, K. Duffy, J. Rosner, Cross-Examination of Witnesses: A Litigator's Puzzle (1989); I. Younger, The Art of Cross-Examination (1976). However, in the interest of time we will only discuss cross-examination in one area -- chain of custody.

For example, a lawyer during cross examination on chain of custody may attack the expert's testimony by showing:

1 — An incomplete foundation for your testimony was laid.
2 — The condition of the evidence is in issue.
3 — The chain of custody laid omits a crucial link.
4 — The link did not use safeguards and violated the regulations or procedure for safeguards.
5 — Substitution may have occurred.
6 — Contamination may have occurred.

At the outset, the lawyer may establish that the sample was fragile and contaminable. To help the jury visualize how delicate the sample is, the lawyer may bring a similar sample into court and, with the court's permission, conduct an in-court demonstration of the malleability of the object. She may have her own expert characterize the substance as delicate and describe the extraordinary measures she takes in her laboratory to guard against contamination. Further, she may ask the court's permission to distribute samples to the jury so that they can "feel for themselves how soft this substance is." Then the lawyer may show that there were nearby sources of contamination, such as storage of samples together, unlocked storage areas, and many people having access to a storage area.

At the conclusion of this type of cross-examination, the lawyer will try to establish that the witness left the sample unattended for a substantial or indefinite time period; while the witness was gone, "someone" moved the sample; and there are discrepancies between the witness' description of the sample and descriptions by prior custodians -- all suggesting that the sample was changed and contaminated.

CONCLUSION

Trace evidence is of considerable importance to lawyers. It is an invaluable type of circumstantial evidence. The expert involved in the examination of trace evidence need be aware of its legal value to the attorney. The expert need also be aware of legal constraints placed on such evidence by the constitution and criminal procedure rules, such as search and seizure, chain of custody, and discovery, so the expert is better able to assist the attorney.

REFERENCES

Illsely, C. P. (1987). Juror attitudes towards fingerprint evidence and the expert fingerprint witness, In: Proceedings of the International Forensic Symposium on Latent Prints, U. S. Govovernment Printing Office Washington, D. C., pp. 155.

Peterson, J., Mihajlovic, S. and Gilliland, M. (1984). Forensic Evidence and the Police: The Effects of Scientific Evidence on Criminal Investigations, National Institute of Justice - Research Report, October.

Peterson, J., Ryan, J., Houlden, P. and Mihajlovic, S. (1986). Forensic Science and The Courts: The Uses and Effects of Scientific Evidence in Criminal Case Processing, Chicago Center for Research in Law and Justice, Univ. IL at Chicago.

TRACE EVIDENCE:
A HOLISTIC VIEW AND APPROACH

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Formal recognition of what we would now call the trace evidence area is a little more than a century old. References to it appear in fiction slightly before they appear in the professional or scientific literature. Palenik has discussed references to trace evidence by Sir Author Conan Doyle in his Sherlock Holmes stories and by the German magistrate Hans Gross in his pioneering book, Handbuch für Untersuchungsrichter (Palenik 1979). There is some speculation that Gross may have gained his insight from reading the Holmes stories. Examples of interesting early cases have also been discussed by Thorwald (1966). In practice, in recent years, the trace evidence area has come to be dominated by hairs, fibers, and to a somewhat lesser extent, paint and glass evidence. In some laboratories the term trace evidence is essentially synonymous with hair and fiber evidence to the degree that this phenomenon has taken the focus away from other types of trace evidence, this is regrettable. Recognition of this imbalance or the relative neglect of other areas of trace evidence is presumably what led the organizers of this symposium and our FBI Laboratory hosts to specify that papers dealing with hair and fiber evidence would not be accepted. Although hairs and fibers certainly have need more research attention, their point is well taken. There are many kinds of trace evidence that remain grossly underexploited and are in need of further attention. These other areas of trace evidence are equally important in their own right. This symposium allows us to focus timely attention on these.

Trace evidence needs to be viewed holistically. This applies to both the way in which the trace evidence area is defined and to the way in which casework is approached. These two manifestations of a holistic perspective are important and will be discussed separately.

Holistic View of what Constitutes Trace Evidence

Trace evidence as a whole occupies a central position in criminalistics. The precise definition of the scope of trace evidence will vary with the region of the country, the laboratory jurisdiction, and the opinion of the particular criminalist queried. However, the scope of trace evidence, even in its most restrictive construction, covers a broad range of materials and evidence types. In broader more holistic views there is little in criminalistics that falls outside of the trace evidence area.

The central role of trace evidence in criminalistics is tacitly recognized by the way in which the American Board of Criminalistics initially set up the five categories of specialization for its Criminalistics Certification Program. Three of the five areas are clearly trace evidence areas. The three are as follows: hairs and fibers, paints and polymers, and fire debris. The two remaining categories are drugs and serology. From a logical and truly holistic perspective even forensic serology can be considered to be a trace evidence area because of the fact that blood and physiological fluids are often transferred in small quantities from surface to another. However, work in this area has become so specialized and the volume of casework so large that we will follow well-established convention and consign this to its own separate area. This will not be the case for some other areas that are often thought to lie outside of the trace evidence dominion.

The use of the word trace as a term applied to this broad evidence category is somewhat arbitrary and requires some explanation. The key concept in our definition of trace evidence has two components. One relates to the contact process that produces the evidence and the other is the small (or trace) amount of material typically transferred. I will use the single term trace evidence to embody the concepts of both trace and transfer evidence.

An argument can be advanced for the inclusion of such pattern evidence as toolmarks, shoeprints and tire marks in the trace evidence category. This is based on the notion of the commonality of a physical contact process as a means of creating or generating the evidence, although it is readily recognized that contact is not always required for the transfer of trace evidence (De Forest *et al.* 1983). In one situation, the material itself, which is transferred as a result of the contact, is what is of concern to us. In the others it is the pattern produced when material transferred (to or from the pattern receiving surface), or it is the pattern of alteration of the topography of one or both of the two surfaces which is of importance. In some cases both the pattern and the nature of the transferred material are important. In these latter situations true dilemmas result which are best resolved with broad trace evidence expertise.

Despite the lack of attention given to the other areas of trace evidence in casework, their importance and need for further development has been recognized for a long time. This is evidenced by the results of two different surveys conducted by Kingston and Brunnelle. The findings of these surveys have been summarized in a Law Enforcement Assistance Administration (LEAA) publication which was a cooperative effort between LEAA and the former National Bureau of Standards (NBS) (Steinberg 1977). In both surveys trace evidence categories represented at least half of the total number of categories. Many were given the highest priorities.

Holistic Approach to the Analysis of Trace Evidence

Trace evidence problems are rarely exactly the same from case to case. The idiosyncrasies of the case and the context in which the evidence is found can be important. Evidence which is crucial in one case may have little or no significance in the next or vice versa. For these reasons a single routine approach cannot be followed. It is necessary to make assessments and plan analytical approaches as the trace evidence examination process proceeds. This calls for the most finely honed thinking and analytical skills of the forensic microscopist or trace evidence examiner. The ability to deal with the vast range of possibilities in the broad trace evidence area requires an extensive knowledge base.

There is a real danger of overspecialization and missing the forest for the trees. This does not imply that the successful trace evidence examiner is an expert in everything. The generalist trace evidence examiner or criminalist must be able to recognize the value of diverse evidence types and make critical assessments to aid in shepherding the evidence to appropriate specialists. There is no question that such specialists are necessary for specialized kinds of testing procedures, but the essential role of the trace evidence generalist in recognizing and assessing evidence and giving direction and form to the scientific investigation cannot be overemphasized. In a small laboratory the generalist will frequently have to refer selected problems to specialists outside his or her own facility. In larger laboratories cross-training of specialists can produce a group of generalists who possess complementary specialities. Irrespective of the system used success with trace evidence depends on the intelligent and informed formulation of the problem before the approach to be used is designed. The process of defining and formulating the problem is intertwined with and dependent on the evidence recognition process. The approach to the analysis and scientific interpretation begins formally in the laboratory but is dependent on accurate information and assessments from the scene and other sources outside the laboratory. This requires the expertise of a scientist with broad knowledge and experience.

TRACE EVIDENCE INTERPRETATION

General Problem Areas

The thesis that, in the past, the major focus has been on hairs and fibers implies that less is done with truly microscopic trace evidence. Truly microscopic trace evidence possesses great potentials and poses challenging problems. A number of questions need to be addressed and considered. It would appear that much such evidence is more-or-less ignored at the present time. For example, how often are particles and other adherent materials on hairs analyzed and utilized in hair comparisons? Such evidence would include hair fixatives and particles characteristic of the environment of the hair donor. The potential for contamination can be expected to become a greater problem with truly microscopic trace evidence. This applies to possible police investigator included contamination and laboratory contamination. There is a need to ask whether there should be more emphasis on having forensic scientists process scenes and whether clean room technology will become necessary for such examinations in the laboratory in the future.

Databases

The lack of information concerning the frequency of occurrence of various items of trace evidence has been a long standing problem plaguing forensic scientists in their attempts to explain the significance of their findings to investigators and attorneys. There is a clear need to develop and maintain databases to provide the information necessary to allow more useful interpretations. Some of this information already exists but is in the hands of manufacturers and either is not available or is not readily available to criminalists. There is no question that substantial costs are associated with the development and maintenance of forensic databases, however, these need not be prohibitive. Cooperative efforts and sharing of information among laboratories nationwide could keep the costs reasonable. Volunteers in one laboratory could receive information about one evidence type from contributors across the country. This could be collated and disseminated in exchange for similar services performed for other evidence types by criminalists in other laboratories.

Proprietary Tracers

Some manufacturers use proprietary trace markers in their products. The forensic science community is not informed as to the extent of this practice and has little data of use in casework examinations of manufactured items. A way of taking advantage of this without compromising the manufacturer's proprietary interests should be explored. Some form of legislation would probably be necessary for accomplishing this.

Environmental Influences

It is important for trace evidence examiners to be aware of the significance of environmental influences on various examples of trace evidence (Chille *et al.* 1987). Such knowledge can be crucial to the examination and proper interpretation of several kinds of trace evidence encountered in casework. Modification and degradation of trace evidence can take place in indoor environments (Chille *et al.* 1988) as well as outdoor ones (Bomardi *et al.* 1987). Bio-degradation is a major factor in both kinds of environment. Examples would include the effects of bacterial, fungal, and insect attack (Chille 1990). The sizable literature on biodegradation can be very useful to criminalists. Sunlight can also cause trace evidence modification and degradation. Special cases, such as root banding with hair, can be of great importance (Petraco 1988). There is a need for more research in these areas.

Retention and Transfer

The significance of trace evidence in many case situations depends on knowledge of retention and transfer properties of the particular items of trace evidence and their interactions with various substrates under specific sets of conditions (Pounds and Smalldon 1975). There is a clear need for more studies to provide data for informed interpretations in this area.

Mechanism of Production of Trace Evidence

Much trace evidence results from the mechanical, chemical, or biological degradation of material from macro world items to produce the finely divided trace materials. Knowledge of the process involved can be important for a complete understanding and proper interpretation of trace evidential items.

Interpretation of Trace Evidence Findings

Many factors can influence the interpretation of findings with respect to trace evidence. Several of these have been mentioned briefly earlier. In addition to environmental influences and questions of retention and transfer, numerical evaluation and statistics play a central role with respect to evidence interpretation. The case context is also of major concern. The same findings in two similar cases may have different interpretations because of differences in details surrounding each of the cases. There is a clear need for scientific input at crime scenes and for early scientific assessment of evidence items submitted to the laboratory as they relate to the case.

In some laboratories additional tests beyond the microscopical and microchemical ones are conducted merely because they are available, because they are expected by the attorney, or because they provide impressive visual or graphical data. The data generated is too often not assessed and made part of the basis for the opinion offered. The resulting charts or other data when presented in court may overly impress jurors. This practice should be very carefully reviewed.

Standards for Testimony

Testimony on trace evidence is some of the most difficult of expert testimony. There are not standards for such testimony. This needs to be discussed explicitly by forensic scientists on an ongoing basis. The establishment of general standards could provide useful guidelines for those charged with the responsibility of giving expert testimony in any of the trace evidence area. In this regard there is an important role to be played by laboratory accreditation and criminalistics certification programs.

TYPES OF EVIDENCE IN NEED OF METHODS DEVELOPMENT

Trace Evidence in Shootings

Trace evidence in shootings takes many forms. Of primary concern are gunshot residue (GSR), material carried by bullets, and marking and material found on bullets.

Gunshot residue on the hands of a suspected shooter and around bullet holes in clothing is analyzed routinely in crime laboratories. Residues on the other surfaces or clothing suspected of being in the region of a gunshot discharge are tested and interpreted less regularly. The methods used for the testing of residues on a suspected shooter's hands forgo pattern information in favor of realistic analysis times. None provides separate data for particulate and non particulate or absorbed residues. It is well recognized that loosely held particulates can be rapidly lost from or redistributed over hand surfaces. Separate sequential testing should be possible and could be expected to provide potentially powerful complementary data. No current methods simultaneously provide definitive identification of GSR and preserve the pattern of distribution. These shortcomings limit the utility of some analyses.

The methods used for testing the pattern of residues around bullet holes evolved little over the last half-century. More attention needs to be paid to extraction efficiency, the specificity of the reactions, and the orientation of the target surface with respect to the gunshot discharge. Knowledge concerning retention of residues under realistic conditions of evidence handling (or mishandling) is lacking.

Methods for analyzing nearby clothing and skin surfaces for residues are jury-rigged and are poorly adapted to the task. In summary, improved methods are needed for all three problem areas of gunshot residue analysis. The retention of particulate residues on hand surfaces has been studied. Little is available in the way of studies which shed light on the retention non-particulate residues on hands or on the retention of any type of GSR on cloth. This is important in questions relating to the identification of the shooter or for meaningful determinations of muzzle-to-target distances. Damage to textile surfaces which are in close proximity to the hot gases produced during a firearm discharge can be seen microscopically. Can a study of such damage of surface modification be used in a complementary fashion with the information derived from residue analysis? This is often ignored in practice. The need for a systematic study of such surface modification is indicated.

More attention needs to be given to the so-called trace metal detection techniques (TMDT) which have been used to address the question of whether or not someone has handled a weapon (Stevens and Messler 1974; Goldman and Thornton 1976). These techniques need more scientific investigation and refinement with respect to implementation and interpretation. They also need to be modified so that they can be interfaced with GSR detection techniques. Another somewhat related problem which needs a scientific approach is the question of how recently a weapon has been fired. Currently the barrel and/or chamber(s) of the weapon is eyeballed to see whether the residues look fresh. Such determination deserve to be put on a firmer scientific foundation. In addition, perhaps the "recently" could be quantified. Some preliminary research two decades ago suggested that this was a good possibility (Franks and Mullen 1972).

Trace evidence along trajectories can be valuable in reconstructions. Bullet wipe is the most commonly encountered example of trace evidence found along bullet trajectories. It is also often the least informative. It consists of residues derived from the ammunition, the bullet itself, the weapon, and lubricants. This material is often wiped off the bullet as it forces its way through the target material. The character of bullet wipe often changes as it passes through successive targets. As might be expected with such successive passage, the contributions of components characteristic of the weapon, primer and propellant are reduced and the bullet itself becomes the major contributor. Other trace evidence can be picked-up, carried, and deposited by bullets as they pass through successive surfaces along their trajectories. Such evidence is often missed. In a recent case, in re-examining some clothing evidence, the author found a collection of fibers and other debris which had been carried and deposited by a bullet. This had been missed by an earlier examiner and provided crucial information with respect to trajectories in the case.

In addition to depositing trace evidence along trajectories, the action of bullets can create characteristic trace evidence from their interaction with and/or alteration of other materials. Such evidence can take the form of lead splash, secondary projectiles, or fused fracture surfaces. Fused fiber ends that are diagnostic of bullet passage through certain textiles will be discussed in a later section.

Trace evidence on bullets when they are recovered can also be of value (Petraco and DeForest 1990). More empirical studies of trace evidence on bullets need to be carried out. At this point certain generalizations can be made. Bullets tend to retain trace evidence that is acquired towards the latter portions of their trajectories. Lead bullets and semi-jacketed bullets are generally better at carrying trace evidence then fully-jacketed bullets as might be expected. Hollow point bullets have obvious advantages in this regard. The lead used in semi-jacketed bullets may be softer than that used in non-jacketed bullets of the same caliber. The effect of the degree of hardness of the bullet lead is not obvious. Softer lead may be more effective for embedding trace evidence but it is also subject to more erosion and loss of trace evidence as the bullet passes through certain surfaces.

There is a clear need to re-think the way in which bullet and cartridge case evidence is routed and analyzed in the laboratory. Much valuable trace evidence is lost in the wax or clay used to mount bullets to the bullet holders of the comparison microscope. This same mounting material can also trace evidence to bullets which are examined subsequently. A similar situation exists with respect to firearms themselves. Potentially valuable trace evidence on weapons is lost when the weapon is sent for functional testing and/or test firing before it is examined by a criminalist.

Pattern evidence on bullets can be used in a similar and complementary manner to that provided by the information derived from trace evidence adhering to bullets. We are concerned here with markings which result from the bullet's interaction with surface along the bullet's path not weapon specific markings resulting form its passage down the barrel. A common example of such pattern evidence would be a textile pattern impressed into the nose of a lead bullet by contact with cloth over a resistant or unyielding surface. Such patterns can be very useful in reconstructions. They can be used to allow an association of a particular object with the bullet in evidence. They can also reveal information about the energy range of the bullet at the time the pattern was acquired, and thus, how much it was slowed by earlier interactions. As was the case with the discussion above relating to the influence of bullet lead hardness on the acquisition and retention of trace evidence by bullets, this factor could have a similar effect on pattern evidence on bullets. This underscores the need to use duplicate or closely similar ammunition in experiments which are conducted to aid in interpretations for a particular case investigation. More research of this type which would be generalizable to many investigations is necessary.

Patterns of muzzle flash and cylinder flash residues and singeing can be very helpful in reconstructions. In favorable circumstances they can be used to fix the position and orientation of the weapon at the moment of discharge.

Paints and Pigments

Even though paints and pigments are analyzed routinely in forensic laboratories, problems in the analysis and interpretation are common place. Gross comparison by instrumental methods is subject to interpretation errors arising from microscale inhomogeneities. Microprobe methods such as selected area electron diffraction (SAED) which focus on single particles or homogeneous domains have the potential of producing definitive identifications of these pure components. However, there are limitations to this approach with respect to providing data relative to significance of the item as associative evidence. Each type of particle in the evidence would have to be characterized and then it would be necessary to produce population statistics for each type for both known and questioned substances in order to compare the overall samples. Because of the extremely time-consuming nature of such an approach, this would be impractical. However, a technique such as SAED would be unrivaled for making fine distinctions between closely related pigments such as different polymorphs.

Trace Evidence in Fires and Explosions

There needs to be more focus on the investigative phase. In this regard bombing scenes are handled fairly well. The need for improvement in scene investigations is especially acute with fires. Scientists seldom get to the scene in fire and arson investigations. Scene assessment and sampling carried out by non-scientific investigators is often inadequate. The truism that the laboratory analysis is only as good as the integrity and relevance of the evidence provided is especially applicable.

Soils

Excellent forensic evidence has been developed utilizing soil in casework for many years. However, many attributes of soils are not taken advantage of in soil comparisons. Some that have been used are not used routinely. For those that are used better databases need to be developed and made available. Studies of retention, transfer, and co-mingling of soil layers on footwear as tracks in soil are being produced, could yield data of help in many cases. Education of forensic scientists is another means of making fuller use of soil evidence.

Glass

The major forensic science activities with respect to glass evidence consist of comparison and reconstruction. More data concerning glass population variations is needed. Recent improvements in the development of elemental analysis approaches have been encouraging. There is a need to develop a computer algorithm to aid in physical matching of both macroscopic and microscopic fragments to fracture surfaces on other pieces. Automation may be an anathema to microscopists and will never replace a skilled microscopical approach, but there is a role to be played by automation and computer technology as an adjunct to the knowledgeable microscopical approach. Reconstructions of fractured glass items can greatly facilitate finding physical fit matches to conclusively prove associations and can be useful in the reconstruction of the fracture itself. For example in experiments that have been done with bullets impacting glass, it appears that impact marks can be made in the very short time interval before the glass actually fractures. It is worth looking for these in fractured glass.

Hairs and Fibers

Although hairs and fibers are, by design, not the subject of this symposium, brief mention will be made of the needs to improve methods for dealing with hair and fiber evidence. More objective approaches to the interpretation of matches for both kinds of evidence need to be developed. The discussion elsewhere in this paper concerning the potential contributions of databases to improved investigations and interpretations is especially appropriate with hair and fiber evidence. These will not be detailed here. This is also true of the need for studies that increase our knowledge of environmental effects as well as transfer and retention characteristics.

Contrived Trace Evidence

The term contrived trace evidence is used to refer to compounds or components added to materials or physical objects to mark them, or objects that come into contact with them, to facilitate future identification or association. Examples would include proprietary traces, gasoline dyes, or the taggant particles (3M) that were required to be added to explosives by manufacturers for a short period of time. Another category would include so-called detective dyes, powders, or pastes. The latter are produced commercially and sold to law enforcement agencies. Unlike the 3M taggants they are not unique and do not provide evidence that is appropriate for use in court. The vendors that supply these do not make this limitation clear. They are useful as investigative aids in developing leads, but do not allow unique associations. Investigators rarely appreciate this distinction. Many products contain only a single fluorescent dye or powder and, as employed, no physical sample is collected and compared. However, it is easy to conceive of ways of producing uniquely coded versions of such products. At one time the New York City Police Laboratory would provide products containing documented mixtures of dyed starch grains to investigators involved in special investigation. A similar idea using mixtures of dyed lycopodium powder grains has been proposed more recently (Kind *et al.* 1978). These ideas should be revived. In any case, it should be made clear to investigators that the commercially available detective powders do not have the ability to provide unique associations. Many investigators seem to be unaware of this until well after they have used one of these products and expended effort in developing a suspect. Without further corroboration the commercial products are of no scientific value at the adjacent level.

Wood and other Vegetable Materials

The major limitation to better utilization of wood and vegetable material evidence would appear to be the training and experience of trace evidence forensic scientists. With more training and education, this problem could be eliminated.

Trace Evidence Produced via the Modification of Materials

Trace evidence can be created through the modification of materials. Several processes are involved. Some take place over very short time frames. It is useful to consider such processes separately from those that involve the mere transfer of trace evidence from one surface to another, although some overlap with respect to this distinction exists.

Several examples of situations where useful trace evidence is produced by rapid, short duration interactions come from cases involving firearms or explosives. One of these is what has been called rapid shear rate fracture of fibers and polymers. With certain polymers and with synthetic fibers such as nylon and polyester bullets passing through them produce characteristic modifications. The ends of fibers around bullets holes in polyester and nylon fabrics have characteristically shaped fused ends. This can be used to definitively identify a questioned hole as a bullet hole even when chemical testing may be ambiguous. Other materials, including metals behave very differently in highly energetic short duration interactions. Metals offering resistance to bullets and front surfaces of bullets themselves often appear to behave as liquids and flow during bullet impacts.

Other changes which take place in the short duration time domain can also produce characteristic physical evidence. The smearing of paints, plastic, and other materials as a result of high pressure contact is one example. Imprint patterns in paint, metal and other materials provide another. The processes which produce there bear further study. Changes which result from transient heating such as melting and singeing from a source such as a flame also need further investigation. Microscale evidence of cutting and crushing of materials can be useful in reconstructions. An understanding of mechanisms is important here as well.

DISCUSSION AND CONCLUSIONS

To take better advantage in the potential inherent in trace evidence several changes or improvements are in order. A holistic view of trace evidence and a holistic approach to its analysis are both necessary for the full potential of trace evidence to be approached.

Knowledge development for two distinct needs should be pursued. The first area would relate to the development of information to facilitate recognition of the evidential value of certain types of trace evidence. The other research need is for the development of comprehensive data for providing useful investigative aids in developing suspects and to establish a basis for the weight to be given to an interpretation in casework after the suspect has been apprehended.

Attention needs to be given to reordering the standard sequence in which evidence is examined in the laboratory. Ideally, the notion of an ordered sequence could be dispensed with entirely and each case could be assessed scientifically prior to deciding on a sequence. Certainly, in most circumstances trace evidence assessments should precede other examinations. Trace evidence on weapons can be lost or compromised if the weapon is test fired before it has been examined for trace evidence. Such problems have been encountered on two recent cases worked by the author.

We need to consider a different approach to the handling of bodies of homicide victims at crime scenes with respect to trace evidence documentation and collection. Shrouds and body bags can be problematic. At outdoor scenes actions by officials arising out of concern for protecting the victim from the gaze of the curious can have a very deleterious impact on trace evidence. Shrouds or sheets placed over the victim's body can add or remove trace evidence and compromise patterns of value for reconstruction purposes. A change in the way such scenes are handled is in order. Trace evidence and pattern evidence should be documented and reserved to the extent possible before the body is placed in a body bag and removed form the scene. Such changes could be expected to make qualitative and quantitative improvements in the value of trace evidence and would also facilitate and enhance reconstruction potentials.

A broadening of the horizons of trace evidence is not without anticipated problems. The resolution of some problems and the development of some new areas will require enhanced resources. There will be a need for improved facilities, training, education, and research. Some improvements can be realized through increased communication and cooperative efforts among forensic scientists. Some will be attained through better training of investigators. Others will require capital expenditures and laboratory staff increases. For example, if we are to take advantage of the potential inherent in truly microscopic trace evidence we may need facilities with clean rooms. We will continually need more research. To avoid compromised evidence we also may need to have scientists at scenes more often. The latter improvement could be expected to enhance reconstructions as well.

SUMMARY

Problems with the examination of trace evidence have been reviewed. It has been pointed out that many kinds of trace evidence are underexploited or even go unexamined. Some casework examiners concentrate their attention on hair and fiber evidence to the exclusion of other less-well appreciated kinds of trace evidence, often to the detriment of case solutions. Recommendations regarding a holistic view of and approach to trace evidence problems have been offered. The need for more research and training as well as the need for the generation and maintenance of databases have been underscored.

REFERENCES

Bombardi, P., Butler, D. J., Hira, B., Adamo, R. A. and De Forest, P. R. (1987). Studies of hair deterioration: exterior environments, presented at the 11th Triennial Meeting Int. Assoc. Foren. Sci., Vancouver, Canada, August 2-7.

Chille, E. A., Gordon, R. E., Adamo, R. A. and De Forest, P. R. (1987). Studies of hair deterioration: interior environments, presented at the 11th Triennial Meeting Int. Assoc. Foren. Sci., Vancouver, Canada, August 2-7.

Chille, E. A., Gordon, R. E. and De Forest, P. R. (1988). Insect damage to hairs and its evidential significance, presented at the 40th Ann. Meeting Am. Acad. Foren. Sci., Philadelphia, PA, February 15-20.

Chille, E. A. (1990). The Forensic Significance of Hair Degradation in Interior Environments, Master's thesis, John Jay College/CUNY, NY.

De Forest, P. R., Gaensslen, R. E. and Lee, H. C. (1983). Forensic Science: An Introduction to Criminalistics, McGraw Hill, NY, pp. 314.

Franks, L. A. and Mullen, R. K. (1972). Time Dependent Electron Magnetic Resonance: Characterization of Detonated Primer Residues, U. S. Dept. Justice, Law enforcement Assistance Administration, National institute of Law enforcement and Criminal Justice, Washington, D. C.

Goldman, G. L. and Thornton, J. L. (1976). A new ferrous metal detection reagent, J. Foren. Sci., 21:625-628.

Kind, S. S., Watson, M., Bland, H. H. and Smith, G. B. (1978). The individuality of tagging powders: The lycode system, J. Foren. Sci. Soc., 18:165-170.

Palenik, S. J. (1979). Microscopy and the law, Ind. Res. Dev., March.

Petraco, N., Graas, C., Callery, F. X and De Forest, P. R. (1988). The morphology and forensic significance of human hair roots, J. Foren. Sci., 33:68-76.

Petraco, N. and De Forest, P. R. (1990). Trajectory reconstructions I. Trace evidence in flight, J. Foren. Sci., 35:1284-1296.

Pounds, C. A. and Smalldon, K. W. (1975). The transfer of fibers between clothing materials during simulated contacts and their persistence during wear: Part II. Fiber persistence, J. Foren. Sci. Soc., 15:29-37.

Steinberg, H. L. (1977). Standard Reference Collections of Forensic Science Materials: Status and Needs, U. S. Dept. Justice, Law enforcement Assistance Administration, National institute of Law enforcement and Criminal Justice, U. S. Government Printing Office, Washington, D. C.

Stevens, J. M. and Messler, H. (1974). The trace metal detection technique (TMTD): A report outlining a procedure for photographing results in color, and some factors influencing the results in controlled laboratory tests, J. Foren. Sci., 19:496-503.

Thorwald, J. (1966). Crime and Science, Harcourt, Brace and World, NY.

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FORENSIC PALYNOLOGY

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The term, palynology was introduced in 1944 by two English men, Hyde and Williams. The "palyn" portion of the word was derived from the Greek verb "Palynein", which translates into the English as the verb "to spread" or "to strew" such as broadcasting seed or fertilizer. This Greek word is closely related to the Latin word "pollen", which means fine flour or dust. The term palynology initially was applied to the study of pollen and spore grains. However, since first introduced, the use of this word has been modified to include other microscopic cyst and cyst-like organisms that have a preservable walled-shell of a chemical composition similar to that of pollen and spores. Because most of these cysts and related organisms are, or initially were, marine in nature, their remains have a more limited application to the forensic sciences.

The first practical study of pollen and spore analysis goes back to 1916. At that time, Lennart Von Post published his study of the compositional changes in the pollen and spores found in samples collected from a Swedish bog. The variations in the pollen and spore assemblages were interpreted as reflecting changes that took place in the vegetation through time. Pollen and spore vegetational changes obtained from northern European cores reflect the amelioration of the climate, the history of the retreat of the European continental glacier, the reforestation and then the subsequent deforestation of the region. These latter mentioned events were brought about with the introduction of agriculture by early man. This history is clearly depicted in the pollen and spore record (Iversen 1949, 1956).

Earlier studies of pollen grains, which range in size from about 10µ to well over 100µ took place soon after the development of the compound microscope. Both the Englishman Nehemiah Grew and the Italian Marcello Malpighi observed and published on pollen grains during the middle of the 17th century. However, long before the morphology of pollen grains was observed microscopically, the biological function of pollen was recognized by the Assyrians in the mid 9th century BC (Wodehouse 1935). An alabaster relief, that originally hung in the palace of Ashurnasirpal II, shows a winged-figure with a birdlike head dusting date-palm flowers with pollen. These people were well aware of the significant role that pollen plays in the fertilization of flowers.

BIOLOGY

Background

Pollen and spores are the reproductive organs of plants. Seed plants liberate pollen grains which contain the male genetic material. These plants retain the female portion of the genetic material in the ovary portion of the pistil. In the lower plants, such as ferns, etc., both the male and the female genetic materials (spores) are shed. These spores can be either unisexual or bisexual.

The genetic material that is shed by both the higher and lower plants is contained within the protoplasm. This material, in turn, is enclosed in a chemically very resistant shell-like material that has been named sporopollenin (Zetsche and Kalin 1928; Zetsche 1929). Protoplasm does not preserve well and it decomposes within a relatively short period of time. The sporopollenin, on the other hand, is a substance that is extremely resistant to all acids, and somewhat less resistant to alkaloids and oxidation. Because of this resistance to chemical attack, fossil pollen and spores have been recovered from rocks that contain the first land plants, rocks that are on the order of 400 million years old (Silurian Period). It is because of this resistance to the chemical destruction of sporopollenin that palynology is a valuable tool in many disciplines, including the forensic sciences.

Production and Dispersion

Other features that make pollen and spores a valuable tool are the great numbers in which they are produced and their method of dissemination. There are two important types of pollen dispersion; one is by animals (zoophilous) and the other by wind (anemophilous). Animal-dispersed pollen is usually generated in relatively small numbers compared to those plants that produce wind-disseminated pollen. There are exceptions, however. Linden, which is an animal-pollinated plant, produces pollen in numbers comparable to those of some wind-pollinated species (Hyde and Williams 1945).

When the animal, whether it be an insect, bat, or bird, is the vector of dissemination, the animal is usually specialized for a group of specific plants. The plant in turn has evolved to make best use of the animal. Zoophilous pollen grains generally are heavily armored with spines or other types of projections. Wind-pollinated plants, on the other hand, depend on the random chance of having the wind disperse enough pollen to find an identical plant species to fertilize. Therefore, these latter mentioned pollen are produced in large numbers and they are dispersed over wide geographic areas. Erdtman (1937) recovered pollen, with the help of a vacuum cleaner, in the middle of the Atlantic Ocean. Stanley (1965b, 1966b, 1969) obtained large numbers of pollen grains from ocean bottom sediments far from shore. Some pollen has even been recovered from middle south Atlantic Ocean sediments thousands of kilometers from their South American source plants (Stanley 1967). Wind dispersed pollen grains usually have a minimum of ornamentation, or they have bladders to make them more buoyant on air currents (Plate 1, Figures 9 and 12). The dissemination of pollen has been studied in detail by Tauber (1965, 1967, 1977) and the reader is referred to these works for more detail on this subject.

Pollen production varies considerably among different plant types. A single anther of hemp (marijuana, a wind pollinated plant) can contain 70,000 pollen grains (Faegri *et al.* 1989). Anyone who ever has had a car parked near a pine tree in the spring can testify as to the large number of pollen that this wind pollinated plant can produce. It is estimated that a single pine tree can produce several hundred million pollen grains a season (Faegri *et al.* 1989).

Morphology

The morphology of pollen and spores usually varies considerably between plant species, genera and families. Because we are dealing with only the resistant outer shell of the grain, all of the morphology is limited to this structure, namely the exine. The exine usually is broken into two subunits called the endexine and the ektexine. The outer layer or shell, the ektexine, contains the sculptural elements and their supporting layer. The ektexine can be either simple or quite complex (Plate 2). There are some types of plants in which there is very little variation and differentiation in the pollen/spore exine morphology. Separation of the pollen and spores of these plants is difficult, if not impossible by the ordinary light-micro- scope. However, scanning and transmission electron microscope studies often can separate species that cannot be differentiated by light-microscope (Stanley and Kedves 1975; Kedves and Stanley 1976). The endexine forms the innermost layer of the exine.

The overall morphology of pollen and spores can be broken into several categories. First there is the morphology of the grain itself. The outline can vary from bean-shape to triangular to circular with many different forms in between. Some pollen types, such as the wind-pollinated conifers, frequently have bladders present to give them additional buoyancy (Plate 1, Figures 1, 9 and 12). Animal dispersed pollen usually has some type of projecting ornamentation, presumably to enable the pollen to latch on to its transporting host.

Secondly, there is the morphology of the aperture . This latter mentioned feature can, in some cases be absent, be slit-like, furrow-like, a pore, or have a combination of both furrows and pores (Plate 1).

Finally, there is the surface morphology or exine sculpture. It can range from smooth to net-like; or it may contain spines, cones, rods, anchors, club-like structures, etc. Identification of a particular plant pollen or spore involves the use of all of these morphological features. This procedure often starts with the examination of the basic shape, followed by the aperture delineation and concluding with a detailed study of the exine sculpturing. The process requires a good compound microscope that has an oil-immersion objective and the capability of achieving total magnifications on the order of 1000 times. As with the study of hairs and fibers, a good reference collection and a comparison microscope should be available to the investigator.

SAMPLING AND PROCESSING

Sampling for pollen and spores can follow the usual collection procedures used for other types of trace evidence such as hairs and fibers. Standard vacuuming with a clean filter insert will catch most of the trace evidence present including the pollen and spores. When sampling boots or shoes, or the underside of a vehicle, one of course is limited to what is available. The sampling of soils presents more difficult problems. Studies (Adam and Mehringer 1975) have shown that a single, or a few, soil samples will not give an adequate representation of the vegetation of the locale. These workers suggest that at least five subsamples are required to characterize the soil surface pollen content of each selected sample stations. They also point out that ten subsample pinches of soil probably would even be better. These pinches of soil can be combined into a single sample for later processing.

The processing of samples for the recovery of pollen and spores can be a tedious task. It is labor intensive and requires facilities that compare in cleanliness to that of a hospital operating room. The various techniques for sampling and processing palynological material are described in detail in such works as Brown (1960), Heusser and Stock (1984), Gray (1965), Moore and Webb (1978), and Low *et al.* (1989).

I remember visiting the palynology laboratory of a major northeastern university several years ago. The scientist was working with 180 million year old (Triassic) pollen and spores and she was interested in showing me some of her material. She was particularly excited about a new discovery she had made. On one of her slides she showed me what she interpreted as a flowering plant pollen grain. This grain was supposedly recovered from sediments that were deposited 100 million years before the first flowering plants are recorded to have appeared on earth. I looked at this pollen and I was amazed to see that it clearly was an birch pollen grain with the protoplasm still intact. As mentioned earlier in this paper, protoplasm is destroyed relatively quickly. The time was spring and it was a nice warm day. The laboratory, located on campus, was in an historic building with 12 foot ceilings. The windows went from the floor to the ceiling and they all were open. I tried diplomatically as I could to suggest to this woman that what she had was contamination from trees outside of her window and not a major scientific discovery. As I remember, she was not very receptive to my suggestion. Science marches on.

In another case, I reviewed a manuscript of an excellent palynologist. His palynological experience was confined totally to the identification of modern pollen. Among his assemblages were some pollen grains that he could not identify. He classified these grains as exotics; that is, species that were introduced into the area from another region or continent. One look at the photographs of these supposed exotics quickly told me that what he was calling exotics were in fact Cretaceous (70 million year old fossil pollen) that were recycled and mixed with his modern forms. This error was pointed out to him and he quickly accepted the criticism and changed his manuscript accordingly.

Contamination is a major problem when working with modern pollen and spores (Stanley 1966a). Therefore, it is necessary to take every precaution to avoid this problem. Containers used for samples must not be reused; glassware and other items used in the processing of these samples must be scrupulously clean. The area in which the material is processed must approach the cleanliness required for aseptic facilities.

A worker in palynology, and especially forensic palynology, clearly has to be able to recognize the presence of contamination in his sample. This contamination can provide some very useful information if it can be shown to be in the original sample and not from the laboratory during processing.

THE APPLICATION OF PALYNOLOGY

Classical Studies

Although the subject of this paper is Forensic Palynology, the current study of pollen and spores is applied to many diverse fields in both the biological and the physical sciences. Each of these areas has an indirect and, in some cases, a direct impact on forensic palynology. Therefore the investigator needs to be aware of them and to understand them. These fields are:

Climatic History (Paleoclimatology): Pollen and spores have been used to record climatic history since palynology was first used. Seventy million year old palm fossils in the rocks of Greenland certainly indicate that the climate in the high latitudes at that time was much warmer than it is today. Whether or not is was as warm as southern Florida, or as warm as Central America, is more difficult to establish. Similarly, it has been shown through pollen and spore analysis that the climate in the western United States became cooler, from a subtropical to warm-temperate climate, about 70 million years ago (Stanley 1960, 1965a). Several thousand year old spruce pollen in areas much farther south than one finds spruce trees growing today indicates that, in the recent past, the climate in these areas was much colder than at present (Hafsten 1985). The change in the climate of an area is determined from its history through time (vertical record) by analyzing core material. However, a similar technique can be used to obtain geographical information (horizontal record). Data, such as published by Delcourt *et al.* (1984) and other workers (Annotated References) are extremely helpful in obtaining useful geographical information. The finding of pollen grains of a plant that grows in either warmer or colder areas on a boot, on the underside of an automobile or its air-filter can be an important piece of evidence pointing to another, earlier location of the boot or vehicle.

The Study of Early Man (Archaeopalynology): The record of man's impact on the local vegetation clearly can be demonstrated by the pollen record. Studies in many areas of both Europe and the Americas show how local forests and other native vegetations were replaced by agricultural crops (Iversen 1949, 1956; Martin and Mehringer 1965). Pollen of certain crops, unique or exotic plants, or forest trees can point to certain vegetational areas where the evidence on hand originally came from. By the same token, it also eliminates many other locales to be considered in the investigation.

Fossil Pollen (Paleopalynology): The term paleopalynology was coined by Stanley (1960 p. 25) to describe the study of pollen and spores recovered from rocks older than the beginning of the last glacial advance (about 1 million years ago). Since the end of World War II, fossil pollen and spores have been widely used in both the oil and the coal industries to date, correlate, and to determine environments of sedimentary deposition. Because of the great economic value of paleopalynology, these industries have significantly advanced the science in the last 45 years. This advancement has been accom-

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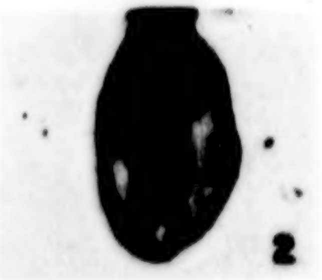
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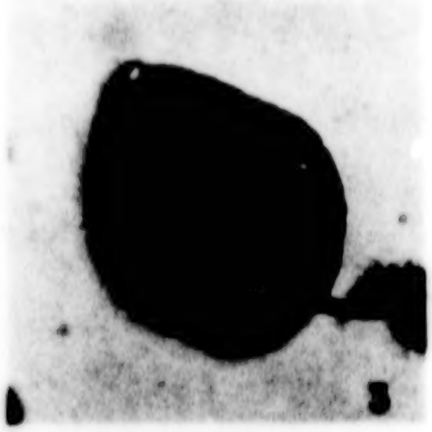
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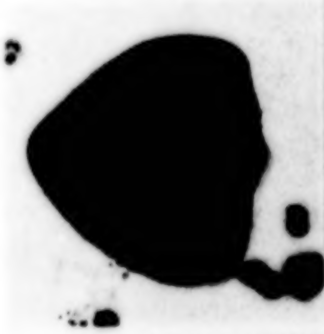
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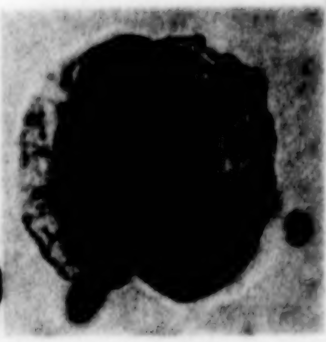
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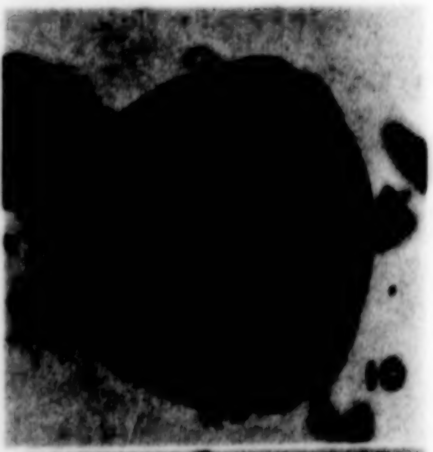
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FIGURE LEGENDS

PLATE 1

Magnification of Figures. 1 and 8-12, c X 530; Figures 2-7, c X 1040, From Stanley (1966a), reprinted with permission of Elsevier Publishing Co., Amsterdam.

Figure 1. Pine pollen — side view showing the two bladders overlapping.

Figure 2. Oak pollen — a pollen grain with three furrows (colpi).

Figure 3. Fossil spore — clearly showing the rugulate ornamentation and the triradiate contact mark. Notice the way this grain accepts stain differently than the grains illustrated in Figures 1 and 2. This type of stain acceptance suggests that this pollen grain has been recycled; that is eroded from older rocks and deposited in younger sediments.

Figure 4. A fossil triporate pollen grain — The three pores are clearly shown in this figure. Note how this pollen grain accepts stain similarly to the one depicted in Figure 3 indicated a similar history.

Figure 5. Another triporate fossil pollen grain — The staining suggests a similar history to those grains illustrated in Figures 2, 3, and 4.

Figure 6. Fossil triporate pollen grain — Even though this grain is recycled from older sediments, it accepts stain naturally. Compare this figure with Figure 1. The interpretation here is that this grain was recycled entombed within a larger piece of sediment so that it was not subjected to oxidation.

Figure 7. A cyst of an unknown marine organism; the age of this specimen is on the order of 200 million years. This fossil probably has been recycled several times. Notice how this grain essentially refuses to accept staining.

Figure 8. Side view of a fossil trilete spore — Observe how then endexine readily accepts the stain whereas the ektexine reluctantly does so. This grain again is considered to be recycled.

Figure 9. A pine pollen grain — these grains together with spruce and fir have a central body with two attached air-bladders. Observe how the body of the grain clearly depicts the differences in the staining of the endexine and ektexine. Compare this figure with Figure 1.

Figure 10. A large triporate fossil pollen grain — Observe the three pores. Also notice the clear staining difference between the endexine and the ektexine. This pollen grain clearly has been recycled.

Figure 11. A large triporate fossil pollen together with a crumpled smaller pollen grain. Occasionally some grains on a slide accept stain more readily than others. The reason for this difference is not entirely clear.

Figure 12. A bisaccate pollen grain — The staining differences of the body can be observed if one looks closely. This pollen grain is considered to be recycled.

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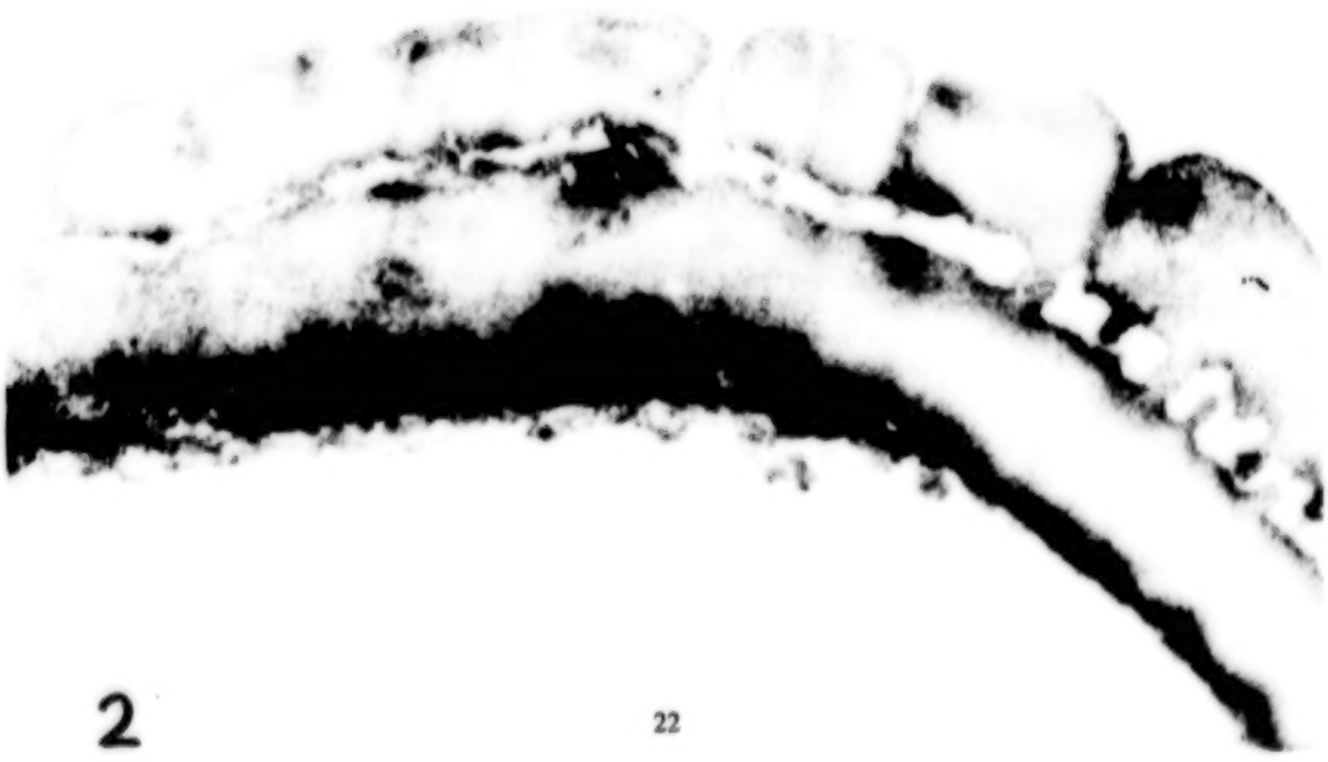

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FIGURE LEGEND

PLATE 2

Transmission electron photomicrographs, magnification X 25,000 Photographs through the courtesy of Prof. Dr. Miklos Kedves, J. A. University, Szeged, Hungary.

Note: The exine layering in pollen grains can best be understood by observing electron photomicrographs through the exine. In this way this knowledge can be related to what one sees with the light-microscope.

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Figure 1. A 60 million year old fossil pollen grain showing a section through a pore; the pore itself (in center of photograph) is clogged with debris. The exine in this case has a roof layer (tectum; the darker layer) underlaid by a relatively thick infratectal layer (the thick lighter colored granular zone). These two layers constitute the ektexine. The much thinner foot layer (the dark thin innermost shell) is the endexine. This illustration shows well how the exine detail can be preserved for an extremely long period of time.

Figure 2. Photomicrograph showing the complex sculptural elements in this 60 million year old fossil pollen grain. This grain contains an outer thick, perforated layer supported by rod-like structures. A relatively thick intermediate shell supports this complex outer structure. All of these structures would constitute the ektexine that one would observe with the light-microscope. The darker colored innermost layer comprises the endexine.

plished through the employment of a large number of palynologists and the funding of considerable research in this area. This support, in turn, has resulted in numerous publications and advancements in the field. The presence of considerably older pollen and spores on a piece of evidence is very important inasmuch as it can lead the investigator to areas where rocks of that age are exposed at the surface. Methods of recognizing such older grains by staining differences have been presented in detail (Stanley 1966a; also, see Plate 1). Other studies (Van Gijzel 1967) have shown that fluorescence can also be used for recognizing such differences. A specific example of how the combination of both fossil and modern pollen in a sample helped solve a criminal case will be presented later.

Honey Analysis (Melissopalynology or Melittopalynology): This term is applied to the pollen analysis of honey. Melissopalynology has been an important source of information for both honey producers and buyers for over 50 years (Zander 1935). The types of pollen found in honey can provide data on the time of the year that the honey was produced (Louveaux 1970). Furthermore, the types of pollen in the honey can pinpoint the geographic region in which the honey was produced thereby exposing illegally imported, or fraudulently labeled honey (Laere et al. 1969; Louveaux et al. 1970, 1979; Crane 1984; Low et al. 1989; Maruizio 1990; Bota 1990; Galimberti 1990).

Other Applications of Palynology: Additional applications of palynology can be found in such disciplines as allergy studies and plant genetics. None of these disciplines currently has any direct important forensic applications.

FORENSIC PALYNOLOGY

Early Applications

Forensic palynology is nothing more than the application of the previously discussed techniques. This topic has been discussed by Stanley (1987), Mildenhall (1988a), Bryant *et al.* (1989), and Palenik (1991). Probably the earliest most recent note on forensic palynology was published by Mildenhall (1982). More recently, Bryant *et al.* (1990) published a general review paper of their earlier oral presentation (Bryant *et al.* 1989). Published reports are available to indicate that pollen and spores have been used to solve criminal cases for many years. For example, Locard (1930 p. 405) mentions pollen as possible physical evidence. He writes "The wind likewise transports pollen dust, whose constant presence is noted on garments and the body during the summer season. It is found in the ears as well as the nostrils where the pollen produces the inflammation called hay fever". Locard (1930) also has done considerable research on mushroom spores in order to help solve poisoning cases. He was well ahead of his time in the application of pollen and spores to forensic science.

The often quoted story that the famous French criminologist Edmond Locard solved a case in the early 20th century by noting the presence of "a spore of an unusual species of dandelion" on a suspect's sleeve (Corre 1968; Cowan 1986) is pure nonsense. It is interesting how such information gets repeated over and over again by people writing about something they know nothing about. First of all, dandelion is a flowering plant of the Chicory group within the Ragweed family and therefore it produces pollen, not spores. Secondly, the size of a dandelion pollen grain is on the order of between 20 to 30µs, something that one could not see without the aid of some magnifying devise. Even a trained palynologist equipped with a good compound microscope would have difficulty to identify such a pollen grain to a specific species because of the great morphological similarity of the pollen grains within this group.

Finally, if one goes back to the original source (Locard 1930 p. 510, Case XVII), one gets quite a different story. Namely that after a body was found in a field, a tramp was picked up because blood stains were noticed on his coat. It was observed that "on one of his sleeves were found winged seeds such as come from dandelions. But these are among the commonest seeds. The microscope examination (of the sleeve), however, disclosed a most unusual combination of substances. There were seeds of a clump of trees situated just a few steps from the site of the crime, and which, carried by the wind, had hooked on the garments of the aggressor during the struggle. This very minute detail solved the problem and the murderer then confessed" (Locard 1930). Notice that there is nothing mentioned in this article by Locard about spores, or the identification of spores with the naked-eye.

There is no doubt that Edmond Locard was a great criminalist and that he was ahead of his time in applying scientific techniques to criminal investigation. However, I don't think that it helps his cause by attributing nonsense to him.

More Recent Case Studies

One: Erdtman (1969 p. 132) reports two cases in which pollen analysis played a crucial role. In 1959 a woman's body was found in the month of June. Evidence pointed to the fact that she had been murdered a month earlier. It was hoped that pollen analysis from the victim's clothing and shoes would be crucial to the case in determining whether or not the victim was killed where the body was found or at some other locale. This case is interesting inasmuch as both the defense and the prosecution each had their own pollen analyst. The analysts both agreed on the pollen and spore composition of both the woman's garments and the soil found at the location. However, they differed on the interpretation of these data. The prosecution pollen expert claimed that the pollen composition of the clothing and the soil did not agree and therefore the body was brought to the site where it was found. The defense palynologist pointed out that the homicide took place in May, a month before the body was found. The vegetation that was producing pollen in June, when the soil samples were collected, was quite different from the May flora of the region. The May vegetation was sparse in grass and weed pollen whereas the summer vegetation was abundant in these pollen types. Erdtman does not state which view prevailed at this trial.

Two: In another case, Erdtman (1969) discusses another homicide. This one took place in Austria in which both modern and fossil pollen on a suspect's shoes helped convict him. A man disappeared in the vicinity of Vienna. Despite an extensive search by the police, no body was found. However, there was a suspect who, subsequently, was brought in for interrogation. The suspect denied having any thing to do with the missing person. Soil taken from the suspect's shoes showed that it contained large amounts of alder and pine pollen. Also present in the soil was some 40 million year old (Oligocene) fossil pollen. A check of both geological and vegetational maps of the region quickly pointed to a single area where both this fossil and this recently produced pollen would be found together. The suspect was taken to this site and he was told that the body was in the region. Being so taken back by the information that the police had, he quickly confessed and took them to a nearby site where the body of the missing man was found.

Three: Hashish found on a suspect trying to enter a New Zealand port was confiscated. The question arose as to whether or not this marihuana resin was a new local source or if it came from a site from outside of the country. Pollen analysis of the resin quickly determined that its pollen composition was not that of New Zealand plants, but from plants primarily growing in Southeast Asia. Palynological evidence established that the hashish was not from a new local source (Mildenhall 1990).

Four: A man was apprehended near a marihuana plantation carrying a small native shrub. The police believed that he was returning from tending to the marihuana whereas the suspect maintained that he was collecting the shrub for his garden. A soil testing kit was taken from the suspect and pollen analysis was performed on the soil still clinging to the probe. These data were compared to those palynological data obtained from the soil on the shrub's roots and soil taken from the marihuana plantation. It was quickly established that the soil from the testing probe and the marihuana plantation essentially contained the same pollen assemblage. On the other hand, the pollen types obtained from the soil on the testing probe were completely different. This palynological information was important in the obtaining a conviction (Mildenhall 1990).

Five: Following a police chase on a muddy New Zealand road, the driver abandoned his motorcycle and fled. A farmer later showed up claiming the bike as his stolen property. The police believed that this person really was the one that they originally were chasing. The suspect claimed that he never had been near the abandoned motorcycle, but that he recently was on a similar muddy road nearby. Pollen analysis was performed on the mud from the his farm, his boots, the muddy nearby road and from the road the motorcycle was found on. Pollen data from the boots and the road where the bike was abandoned were essentially the same. On the other hand, the pollen composition of the farm mud and the mud from the nearby road were different thereby implicating the farmer (Mildenhall 1990).

Six: Faegri *et al.* (1989) mention a case in which straw had been substituted for an expensive item in a shipping crate. Analysis of the pollen contaminating the straw indicated that the original locale of the straw and, therefore, where the substitution supposedly took place.

Seven: Mildenhall (1988b) mentions still another case where palynology was instrumental in solving a criminal case. The incident involved the theft of deer velvet from a New Zealand exporter. Deer velvet is a thin layer of fur that grows on the antlers and it is harvested yearly from domestic deer for export. It is sold in Asia because it is believed to have medicinal properties. Several thousand dollars worth of this velvet was removed from a warehouse. Subsequently a suspect was found in possession of a large quantity of velvet. He claimed that he had acquired this supply from naturally shed velvet in the woods from wild deer. Pollen analysis of both the soil samples collected from the deer farm and from the woods where the suspect said that he collected the velvet clearly showed that the velvet in question came from the deer farm and not from the woods.

Eight: Other types of forensic palynological studies recently have been taken in the New York City Police Laboratory. Several years ago at the Annual Meeting of the American Society of Crime Laboratory Directors, I had a conversation with one of the directors of a U. S. Customs Lab. He was bemoaning the fact that Asian coffee was coming into the United States under the guise of South American coffee and they had no way to tell the difference. I pointed out that one quick way to determine the source of the coffee was to look at the pollen contaminating it. Certainly, the vegetation of southeastern Asia is different than that of South America. He thought that this was a good idea; whether or not this suggestion was ever pursued, I do not know.

That discussion got me to thinking that the same technique also could be applied to drugs such as heroin and cocaine (Stanley 1987). Administrative duties kept me from following up on this idea until recently (Stanley 1992). The Drug Enforcement Agency Research Laboratory in Virginia attempts to determine the country of origin of drugs. My understanding is that the method they use is to analyze the processing technique used to make the drugs. So that if a clandestine laboratory in the Caribbean uses the same processing technique as a southeastern Asian laboratory, they conclude that the drugs came from the Asian source.

In an attempt to put my idea into practice, over 124 g of cocaine hydrochloride, destined for destruction, were put into solution in 400 ml of methanol. The solution then was centrifuged and the residue examined. Three distinct pollen and spore assemblages were recognized on their staining characteristics (Stanley 1966a). The first assemblage is interpreted as being contamination when the cocaine was being processed in South America. The second represents pollen that was introduced when the packaging was opened in this country for either cutting or repackaging. The third assemblage is interpreted as contamination while the cocaine was being processed for palynological examination in the Police Laboratory.

From the palynological data, it was concluded that the cocaine was processed in South America during their spring. The following year, spring in the U.S., the sample was opened in a restricted area of the U. S. (or Canada) where scrub pine and hemlock are found growing together (Stanley 1992).

I am excited about these results because the indigenous pollen and spores can tell what part of the world the drugs originally came from. It is also possible that the contaminating pollen and spore content may be able to indicate in what part of this country these drugs were cut or repackaged. This information can be very important intelligence data for both drug interdiction and enforcement. Furthermore, these types of studies can open up a completely new area within the field of palynology. This preliminary study will be pursued with additional cocaine samples; heroin analysis will also be added to this study.

CONCLUSIONS

Forensic palynology is not the cure-all for criminal cases. However, it can provide some very useful information in certain instances. As with any sort of trace evidence, care in collecting, proper assurance of the chain-of-custody, and the analysis by properly trained personnel in an adequate facility are basic necessities.

The forensic palynologist should be well-trained not only in modern pollen and spores, but also the fossil ones. A good understanding of geology, botany, ecology and plant geography is essential.

Fossil pollen and spores can be found in many forensic samples. There have been several cases in the past where workers have failed to recognize fossil pollen grains in their investigations. These fossil grains were interpreted as exotics thereby resulting in serious mistakes. Unfortunately, the information on fossil pollen and spores is widely scattered throughout the literature with no one good single reference being available at this time. The publications listed by Potonie are probably the best works for one to start with in order to get a good feel for the morphological types that can be encountered with fossil grains. Nevertheless, if used correctly by properly trained people, palynology can, and should, be another useful tool to be added to the criminalist's investigative arsenal.

ACKNOWLEDGMENTS

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CITED REFERENCES

Adam, D. P. and Mehringer, P. J,. Jr. (1975). Modern pollen surface samples- An analysis of subsamples, J. Res. U. S. Geol. Surv. 3:733-736.

Bota, H. (1990). Identification of pollen grains in honey, Honeybee Sci. 11:3.125-128.

Brown, C. (1960). Palynological techniques, Privately published, Baton Rouge, LA.

Bryant, V. M., Jr., Jones, J. G. and Mildenhall, D. C. (1989). Forensic Palynology in the United States of America. Presented at the 22nd Annual Meeting of the Am. Assoc. of Strat. Palynol., Tulsa, OK.

Bryant, V. M., Jr., Jones, J. G. and Mildenhall, D. C. (1990). Forensic palynology in the United States of America, Palynology 14:193-208.

Corre, F. (1968). Profile of Edmond Locard, The Criminalist, 3:119-129.

Cowan, M. E. (1986). Trace evidence, tremendous trivia, the relativity of significance, In: Forensic Science (Davies, G., ed.). Am. Chem. Soc., Washington, D.C., pp. 347-372.

Delcourt, P. A., Delcourt, H. R. and Webb III, T. (1984). Atlas of mapped contributions of dominance and modern pollen percentages for important tree taxa in eastern North America, Am. Assoc. Strat. Palynol. Contrib. Ser. 14.

Erdtman, G. (1937). Pollen grains recorded from the atmosphere over the Atlantic, Meddel. Goteb. Bot. Tradg. 12:186-196.

Erdtman, G. (1969). Handbook of palynology, Munksgaard, Copenhagen.

Faegri, K., Iversen, J., Kaland, P. E. and Krzywinski, K. (1989). Textbook of Pollen Analysis, IV edition, John Wiley and Sons, NY.

Galimberti, P. (1990). Le analisi palinologiche del miele (Pollen analysis of honey), Ape Nostra Amica. 12:3.5-9.

Gray, J. (1965). Palynological techniques, In: Handbook of Paleontological Techniques, (Kummel, B. and Raup, D., eds.), W. H. Freeman and Co., San Francisco, pp. 471-706.

Grew, N. (1682). The anatomy of plants, London.

Hafsten, U. (1985). The Immigration and spread of spruce forests in Norway, traced by biostratigraphical studies and radiocarbon dating: A preliminary report, Nor. Geogr. Tidsskr. 39:99-108.

Heusser, L. E. and Stock, C. E. (1984). Preparation techniques for concentrating pollen from marine sediments and other sediments with low pollen density, Palynology 8:225-227.

Hyde, H. A. and Williams, D. W. (1944). Right word, Pollen Anal. Circ. 8:6.

Hyde, H. A. and Williams, D. W. (1945). Pollen of lime (Tilia sp.), Nature 155:457.

Iversen, J. (1949). The influence of prehistoric man on vegetation, Dan. Geol. Unders. 4:3.

Iversen, J. (1956). Forest clearance in the stone age. Sci. Am. 194:36-40.

Kedves, M. and Stanley, E. A. (1976). Electron-microscopical investigations of the Normapolles group and some other selected European and North American angiosperm pollen, Part II, Pollen et Spores. 18:105-127.

Laere, O. van, Lagasse, A. and Mets, M. de (1969). Use of the scanning electron microscope for investigating pollen grains found in honey samples, J. Apic. Res. 8:3.139-145.

Locard, E. (1930). The analysis of dust traces, Part III, Am. J. Police Sci. 1:496-514.

Louveaux, J. (1970). Atlas photographique d'analyse pollinique des miels. Minist. Agric. Serv. 3. (Photographic atlas for pollen analysis of honey).

Louveaux, J., Maurizio, A. and Verwohl, G. (1970). Methods of melissopalynology, Bee World 51:125-138.

Louveaux, J., Maurizio, A., Verwohl, G. (1979). Methods of melissopalynology, Bee World 59:139-157.

Low, N. H., Schweiger, C. and Sporns, P. (1989). Precautions in the use of melissopalynology, J. Apic. Res. 28:1.50-54.

Malpighi, M. (1687). Opera omnia. London.

Martin, P. S. and Mehringer Jr., P. J. (1965). Pleistocene pollen analysis and biogeography of the southwest, In: The Quaternary of the United States (Wright, H. E., Jr. and Frey, D. G., eds.). Princeton University Press, pp. 433-451.

Maurizio, A. (1975). Microscopy of honey, In: Honey, a comprehensive survey (E. Crane, ed.), Cornell Univ. Press, pp. 240-257.

Mildenhall, D. C. (1982). Forensic palynology, Geol. Soc. New Zealand Newsletter. 58:25.

Mildenhall, D. C. (1988a). Forensic palynology in New Zealand, Presented at the Forensic Palynology Symposium in conjunction with the 7th Internat. Palynol. Cong., Brisbane, Australia.

Mildenhall, D. C. (1988b). Deer velvet and palynology: An example of the use of forensic palynology in New Zealand, Tuatara 30:1-11.

Mildenhall, D. C. (1990). Forensic palynology in New Zealand, Rev. Paleobot. Palynol. 64:227-234.

Moore, P. D. and Webb, J. A. (1978). Pollen analysis, John Wiley and Sons, NY.

Palenik, S. (1991). Isolation, identification, and interpretation of pollen grains from casework- sized soil samples, Presented at the 43rd Annual Meeting, Am. Acad. Foren. Sci. Anaheim, CA.

Stanley, E. A. (1959). Some observations on the geniculus in the pollen of *Quercus prinoides*, Micropaleont. 5:351-354.

Stanley, E. A. (1960). Upper Cretaceous and lower Tertiary sporomorphae from northwestern South Dakota. Ph.D. Dissertation, Penn. State Univ. (L.C. card no. Mic. 60-5461) Univ. Microfilms. Ann Arbor, Mich. Dissertation Abstr. 21: 1914-1915 (1961).

Stanley, E. A. (1965a). Upper Cretaceous and Paleocene plant microfossils and Paleocene dinoflagellates and hystrichosphaerids from northwestern South Dakota, Bull. Am. Paleont. 49:175-384.

Stanley, E. A. (1965b). The abundance of pollen and spores in marine sediments off the eastern coast of the United States, Southeastern Geol. 7:1.25-33.

Stanley, E. A. (1966a). The problem of reworked pollen and spores in marine sediments, Marine Geol. 4:397-408.

Stanley, E. A. (1966b). The application of palynology to oceanology, Deep Sea Res. 13:921-939.

Stanley, E. A. (1967). Palynology of six ocean bottom cores from the southwestern Atlantic Ocean, Rev. Palaeobot. Palynol. 2:195-203.

Stanley, E. A. (1969). Marine palynology, In: Oceanogr. Mar. Biol. Ann. Rev. (Barnes, H., ed.) George Allen and Unwin Ltd., London, pp. 277-292.

Stanley, E. A. (1987). Palynology as physical evidence, Presented at the 13th Annual Meeting of the Northeastern Assoc. of Foren. Sci., Princeton, NJ. pp. 12-13.

Stanley, E. A. (1992). Application of Palynology to establish the provenance and travel history of illicit drugs, The Microscope 40:149-152.

Stanley, E. A. and Kedves, M. (1975). Electron-microscopical investigations of the Normapolles group and some other selected European and North American angiosperm pollen, Part I. Pollen et Spores. 17:233-271.

Tauber, H. (1965). Differential pollen dispersion and the interpretation of pollen diagrams, Dan. Geol. Unders. 2:89.

Tauber, H. (1967). Investigations of the mode of transfer of pollen in forested areas, Rev. Palaeobot. Palynol. 3:277-286.

Tauber, H. (1977). Investigations of aerial pollen transport in a forested area, Dan. Bot. 32:1.

Van Gijzel, P. (1967). Palynology and fluorescence microscopy, Rev. Palaeobot. Palynol. 2:49-79.

Von Post, L. (1916). Om skogstradpollen I sydsvenska torfmoss- lagerfoljder, Geol. Foren. Stockh. Forh. 38:384-390.

Wodehouse, R. P. (1935). Pollen grains. McGraw-Hill, NY.

Zander, E. (1935). Blutengestaltung und Herkunftbestimmung bei Blutenhonig, Berlin.

Zetsche, F. (1929). Die chemischen Grundlagen der Pollenanalyse, Mitt. naturforsch. Ges. Berlin.

Zetsche, F. and Kalin, O. (1928). Untersuchungen uber die Membran der Sporen und Pollen, Justus. Liebigs. Ann. Chem. 461: 89-107.

ANNOTATED USEFUL REFERENCES

The literature on palynology and plant geography is abundant. It is realized that workers in the forensic field who want to use palynology in their work may not be acquainted with the reference literature available. Therefore, an attempt is made to include and briefly annotate some of the more important reference books and monographs in the field. There are many shorter publications in a whole host of botanical, geological, ecological and other scientific journals. These publications usually consist of detailed studies of a single, or a group of species, as for example in Stanley 1959, Stanley and Kedves 1975, and Kedves and Stanley 1976. The works that list individual species, or groups of species, are too numerous to list here. The reader is referred to the bibliographies in such recent works as Faegri *et al.* (1989), or to some of the regional monographs that follows. The older volumes included in this list may be out of print but they should be available in many university libraries.

ANNOTATED REFERENCES

Basset, I. J., Crompton, C. W. and Parmelee, J. A. (1978). An atlas of airborne pollen grains and common fungus spores of Canada, Monograph No. 18, Canadian Department of Agriculture, Ottawa, Canada. This volume covers pollen and fungal spores of 145 plants. Included are photographs, descriptions and the flowering period for each species covered. Although the volume is intended for Canadian use, certainly the same species can be found in the northern portions of the U. S.

Beug, H. J. (1961). Leitfaden der Pollenbestimmung, Lief I. Fischer, Lieberts-Stuttgart, Germany (Manual for pollen identification). In German, but many good photographs of some central European pollen. Unfortunately, only part I of this series was published.

Boros, A. and Jari Komlodi, M. (1975). An atlas of recent European moss spores, Akademiai Kiado, Budapest. A useful reference to European moss spores with 273 plates; in English.

Brown, C. A. (1960). Palynological techniques, Privately published. Baton Rouge, LA. This handy little book combines under one cover just about all of the palynological processing methods published up to 1960. It was privately published and may be difficult to obtain.

Burns, R. M. and Honkala, B. H. (1990). Sylvics of North America; Vol. 1, Conifers, U. S. Government Agricultural Handbook 654, U. S. Government Printing Office, Washington, D. C.

Burns, R. M. and Honkala, B. H. (1990). Sylvics of North America; Vol. 2, Hardwoods, U. S. Government Agricultural Handbook 654, U. S. Government Printing Office, Washington, D. C. These two massive volumes by Burns and Honkala update E. L. Little's and Fowells' important works.

Crane, E., Walker, P. and Day, R. (1984). Directory of important world honey sources, Internat. Bee Res. Assoc. London. A volume that is indispensable for the honey palynologist. The work lists 467 worldwide plants that are important sources honey. In addition, details are listed on the plants flowering period and publications where specific pollen descriptions for these plants can be found.

Cranwell, L. M. (1953). New Zealand Pollen Studies, The Monocotyledons. Bull. No. 3, Auckland Insti-

tute and Museum, Harvard University Press. A good review of the monocots from this region of the world.

Erdtman, G. (1952). Pollen morphology and plant taxonomy, Angiosperms- An Introduction to Palynology, Vol. I. Chronica Botanica, Waltham, MA. This volume is the first of a four part series. It is a very valuable reference book that should be in the library of every serious worker in the field.

Erdtman, G. (1954). An introduction to pollen analysis. Chronica Botanica, Waltham, MA. A general volume that is intended as an introductory text to the subject rather than a reference volume. It contains a large number of line drawings of pollen and spores that give the reader a general idea about their morphology. This volume should not be used as the only source for identification.

Erdtman, G. (1957). Pollen and spore morphology/plant taxonomy, Gymnospermae, Pteridophyta, Bryophyta, An introduction to palynology, Vol. II. Chronica Botanica, Waltham, MA. See Erdtman, G. 1952.

Erdtman, G. (1965). Pollen and spore morphology/plant taxonomy, Gymnospermae, Bryophyta (Text), An introduction to palynology, Vol. III. Almqvist and Wiksell. Stockholm. See Erdtman, G. 1952.

Erdtman, G. (1969). Handbook of palynology, Munksgaard, Copenhagen. This volume is more or less an update of Erdtman's 1954 text. It is a good introductory book that covers palynology as well as other types of organic-walled organism. As previously indicated for his 1954 book, this text should not be used as the only source for identification.

Erdtman, G. and Sorsa, P. (1971). Pollen and spore morphology/plant taxonomy, Pteridophyta, An introduction to palynology, Vol. IV. Almqvist and Wiksell, Stockholm. See Erdtman, G. 1952.

Faegri, K., Iversen, J., Kaland, P. E. and Krzywinski, K. (1989). Textbook of Pollen Analysis, IV edition, John Wiley and Sons, NY. This book is an up-to-date edition of the authors' earlier texts. It is a superb introductory book for palynology. In addition, it contains a first-class key to the genera and a more than adequate glossary. It is an expensive volume, but a must for the serious worker.

Fowells, H. A. (1965). Silvics of forest trees of the United States, U. S. Department Agriculture Handbook 271, Washington, D. C. This monograph contains distribution maps of the major trees of the U. S.

Gray, J. (1965). Palynological techniques, In: Handbook of Paleontological Techniques, (Kummel, B. and Raup, D., eds.), W. H. Freeman and Co., San Francisco, pp. 471-706. This reference text contains an expanded chapter on the various newer techniques for all types of palynological applications. This work supplements Brown, 1960.

Harris, W. F. (1955). A manual of the spores of the New Zealand Pteridophyta, Dept. Sci. and Indus. Research Bulletin 116. Wellington. A useful reference to southern hemisphere spores.

Haug, T. C. (1972). Pollen flora of Taiwan. National Taiwan University, Taipei. An important reference to southeastern Asia pollen; contains 177 plates. In English.

Haug, T. C. (1981). Spore flora of Taiwan, National Taiwan University, Taipei. An important guide to the southeastern Asian spores; this volume supplements Haug, 1972.

Heusser, C. J. (1971). Pollen and spores of Chile. University of Arizona, Tucson. A good guide to the pollen and spores of South America; this work contains 60 plates illustrating the more common South American pollen and spore types.

Hodges, D. (1952). The Pollen loads of the honeybee, Bee Research Assoc., London. This is an interesting little volume that should be in the library of anyone working with bees or honey. There are line drawings of common English pollen types typically associated with bees and honey.

Hyde, H. A. and Adams, K. F. (1958). An atlas of airborne pollen grains. Macmillian and Co., London. This book contains many excellent photographs of the more common English pollen associated with hayfever. A key for identification and a glossary are included.

Ikuse, M. (1956). Pollen grains of Japan, Hirokawa, Tokyo. In Japanese; however, the 76 plates are of good quality which make this work a useful guide to southeastern Asian pollen.

Kapp, R. O. (1969). How to know pollen and spores, William C. Brown Co., Dubuque, IA. A handy little volume for the cursory identification of pollen and spores. The descriptions are rather brief and this book should not be used sole as a source for identification. The book does give one a good overview of the various types of morphologies one is likely to encounter in pollen and spores.

Lewis, W. H., Vinay, P. and Zenger, V. E. (1983). Airborne and allergenic pollen of North America, The Johns Hopkins University Press, Baltimore. An important work that contains many excellent photographs. In addition, this volume has extensive distribution maps for all of the major plant species including weeds and herbs. A must for the serious worker.

Little, E. L., Jr. (1971). Atlas of United States trees, Vol. 1, conifers and important hardwoods, U. S. Department of Agriculture Misc. Pub. 1146. Washington,

D. C. An important reference containing maps showing the distribution of trees within the U. S.

Little, E. L. Jr. (1976). Atlas of United States trees, Vol. 3, minor western hardwoods, U. S. Department of Agriculture Misc. Pub. 1134. Washington, D. C. See Little, 1971, for comments.

Little, E. L., Jr. (1977). Atlas of United States trees, Vol. 4, minor eastern hardwoods, U. S. Department of Agriculture Misc. Pub 1342. Washington, D. C. See Little, 1971, for comments.

Moore, P. D. and Webb, J. A. (1978). Pollen analysis, John Wiley and Sons, NY. An excellent introductory palynology text. This volume contains many good photographs, an adequate key for identification and an excellent glossary. In addition, there is a very good chapter on the collection and treatment of palynological samples.

Nair, P. K. K. (1965). Pollen Grains of Western Himalayan Plants, Asia Monographs No. 5. Asia Publishing House, London. One of the few works on the palynology of this region. The monograph contains pollen keys, line drawings and photographs.

Nilsson, S., Praglowski, J. and Nilsson, L. (1977). Atlas of airborne pollen grains and spores of northern Europe, Ljungforetagen, Orebro, Sweden. This monograph contains distribution maps for the more important vegetational types of northern Europe; contains 74 plates, text, and a good glossary.

Pla Dalmau, J. M. (1961). Pollen, Madrid. This work consists of line drawings with the descriptions in Spanish. A useful reference for southern European pollen and spores.

Potonie, R. (1956). Synopsis der Gattungen der Sporae dispersae, Teil I, Beih. Geol. Jahrb. 31. This work by Potonie, and the two following volumes, although somewhat out of date and in German, are one of the better introductions to the genera of fossil pollen and spores.

Potonie, R. (1958). Synopsis der Gattungen der Sporae dispersae, Teil II, Beih. Geol. Jahrb. 39. See Potonie, 1956.

Potonie, R. (1960). Synopsis der Gattungen der Sporae dispersae, Teil III, Beih. Geol. Jahrb. 41. See Potonie, 1956.

Ronbik, D. W. and Moreno Patino, J. E. (1991). Pollen and Spores of Barro Colorado Island, Monographs in Systematic Botany, Vol. 36, Missouri Botanical Garden. An important tropical, Central American palynological study of a Panamanian Nature Preserve. This work includes identification keys, descriptions and 97 plates.

Sawyer, R. (1981). Pollen identification for bee keepers, University of Cardiff Press, Cardiff, U. K. Tabulated keys for 134 British pollen types.

Selling, O. H. (1946). Studies in Hawaiian pollen statistics, Part 1, Spores of Hawaiian Pteridophytes, Bishop Museum Spec. Pub. 37. Honolulu. An important reference for Hawaiian palynology.

Selling, O. H. (1947). Studies in Hawaiian pollen statistics, Part 2, The Pollens of the Hawaiian Phanerogams, Bishop Museum Spec. Pub. 38. Honolulu. See Selling, 1946, for comments.

Viereck, L. A. and Little, E. L., Jr. (1975). Atlas of United States trees, Vol. 2, Alaska trees and common shrubs, U. S. Department of Agriculture Misc. Pub. 1293, Washington, D. C. See Little, 1971, for comments.

Wodehouse, R. P. (1935). Pollen grains. McGraw-Hill, NY. All serious workers should have this book in their library. Although published in 1935 by the pioneer of American palynology, the volume contains a wealth of information that still is current.

Wodehouse, R. P. (1945). Hayfever plants, Chronica Botanica, Waltham, MA. A general survey of the hayfever plants and their pollen.

PARTICLE ANALYSIS BY THE SCANNING ELECTRON MICROSCOPE

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It is a well established forensic practice to sample a shooter's hands to analyze for the presence of smoke and other particulates ejected from a firearm, collectively referred to as gunshot residue (GSR) (Andrasko and Maehly 1977; Wolten *et al.* 1977, 1978, 1979abc). Particle analysis involves the search for, and characterization of individual GSR particles, typically 0.5 to 10 m in diameter. It is the individual analysis of each particle that differentiates particle analysis from bulk analysis. The major advantage of particle analysis is its sensitivity and specificity for GSR. The three critical GSR elements: lead, antimony and barium, are detected and localized within the particle and thus are shown to be in association. Furthermore, the particle morphology is available for inspection, which constitutes a test independent of and complementary to elemental analysis. Bulk methods generally involve the determination of the weight of the principal GSR elements in a dissolved sample. The elements are only presumed to be associated. The major drawback to particle analysis is the requirement for expensive instruments: a scanning electron microscope (SEM) and energy dispersive x-ray spectrometer (EDX), or less commonly, a wavelength dispersive x-ray spectrometer (WDX). Furthermore, the particle analysis method generally requires more time to process each sample.

PARTICLE CLASSIFICATION

Particles are classified according to their composition and morphology into three broad groups: unique, consistent and unrelated. Unique particles are those for which no source is known other than the discharge of conventionally primed ammunition. Unrelated particles are those known or presumed not to be associated with the discharge of ammunition. The third category, consistent particles, are known to be produced by the discharge of ammunition but alternate sources have been identified.

Compositional criteria for unique particles from conventional ammunition were given by Wolten *et al.* (1977) as:

Pb Sb Ba
Sb Ba
Ba Ca Si with trace S

The particles were also allowed to contain any combination of Si, Ca, Al, Cu, Fe, S, P, Zn, Ni, K and Cl, except that the peak height of zinc must be less than that of copper, and nickel must be in combination with zinc and copper. Tin was also allowed in the event that obsolete ammunition was encountered. Their list was derived from a study of particles collected from test firing an assortment of firearms and ammunition types, and from occupational or environmental sources where the metals lead, barium and antimony were liable to be melted or vaporized. The list was revised in Wolten *et al.*'s 1978 Addenda and Errata to the following:

Pb Sb Ba
Sb Ba
Ba Ca Si with trace S
Ba Ca Si with trace Pb, Cu Zn absent

Later work by Wallace and McQuillan (1984) suggests that the two Ba Ca Si classes should be treated with great caution, if not removed from the unique category. They noted on three separate occasions that casework samples containing Ba Ca Si trace S particles were accompanied solely by lead particles. This is not consistent with the range of compositions expected from primers containing Pb Ba or Pb Ba Sb. That, and owing to the commonness of barium, calcium and silicon in the environment, they concluded that the Ba Ca Si particles in those samples were unlikely to have originated from the discharge of a primer. Otherwise their particle classification system is harmonics with that of Wolten *et al.* (1977). They also include sodium and magnesium in the list of allowed elements, but at the trace level only (see Table 1).

The ideal GSR particle is spherical in shape. However, morphology is typically treated as subsidiary to elemental composition, so that any spherical or rounded shape that has the appearance of having been melted or otherwise exposed to heat is acceptable. A crystalline morphology or features of crystal fragments would be cause for elimination as a unique particle.

Wolten *et al.* (1977) give the compositional criteria for consistent particles, sometimes referred to as supporting or indicative particles, as follows:

Pb Sb
Pb Ba
Pb
Ba if S absent or trace
Sb (rare)

The list was later revised by Wolten *et al.* (1978) and renamed to characteristic particles, presumably meant

Table 1. REVISED COMPOSITIONAL AND MORPHOLOGICAL CLASSIFICATION RULES

UNIQUE	(Non-crystalline morphology, especially if spheroidal or of non-uniform composition
Pb Sb Ba	
Sb Ba	
Ba Ca Si trace S	(interpret with caution)
Ba Ca Si trace Pb, Cu Zn absent	
CHARACTERISTIC	(morphology same as for unique particles)
Pb Sb	
Pb Ba	
Pb if Fe, P absent	
Ba if S absent or trace	
Sb (rare)	
ALLOWED ELEMENTS	
Si Ca Al Cu Fe S P Zn (Cu > Zn) Ni (only with Cu, Zn) K Cl Na (trace) Mg (trace) and other elements if known to be in the ammunition connected with the shooting.	

to emphasize that the composition is very suggestive of GSR although not unique to it. The compositional criteria are the same except that the lead particles must be free of iron and phosphorous. Having a spherical morphology enhances the characteristic attribute. The list of additional allowed elements specified for the unique particles also applies to the characteristic category.

Unrelated or inconsistent particles are assumed to be occupational or environmental particles which happen to be on the skin at the time of sampling. Although this category is generally ignored, a few interesting observations can be made. Barium-sulphur particles, when barium and sulphur are major components, are excluded as being GSR. Since both barium and sulphur are major components of conventional priming mixes, barium-sulphur particles would not be an unexpected product. It would appear that they are eliminated to err on the side of safety, since barium-sulphur compounds appear in many consumer products. Antimony, in the absence of sulphur, may become a similar candidate for elimination since antimony oxide is used as a fire retardant in fabrics.

ANALYSIS OF PARTICLE POPULATIONS

In conventional ammunition the unique particles originate from the primer. Consequently they are unique to the discharge of primers, even though they might contain material from other parts of the ammunition. Other varieties of ammunition used in cartridge powered industrial tools, blank firing guns and the like, which employ similar primers, can also generate the same unique primer particles (Wallace and McQuillan 1984; Wallace 1986). The characteristic and consistent populations are a product of the discharge of the entire cartridge, principally from the primer, cartridge case and projectile, individually or in combination. It is axiomatic to say that the presence or absence of unique particles determines the presence or absence of GSR. In order to unequivocally establish the presence of GSR, at least one unique particle must be located and characterized. However, it is still useful to examine the non-unique population.

Supporting particles are found in GSR deposits in vastly greater numbers than unique particles. Wallace (1986) reports a ratio of 35:1. Merely establishing that a supporting particle population exists would be evidence that the normal mechanisms of GSR production were at work. Finding a population of unique particles in the absence of characteristic or consistent particles would be an unusual and suspicious circumstance.

Particle populations from cartridge powered industrial tools are reported by Wolten *et al.* (1977) and by Wallace and McQuillan (1984) to contain particles which would otherwise be classified as unique, that contain inconsistent metals such as chromium and manganese, and zinc with inconsistent zinc-copper ratios. However, not every lead-antimony-barium or antimony-barium particle was found to contain the contra- indicative elements. The remaining lead-antimony-barium and antimony-barium particles which did not contain the contra-indicative elements, when viewed independently as individual particles, were necessarily classified as unique. When viewing a population such as this, it would be necessary to examine the supporting particle population carefully to determine whether the residue arose solely from the discharge of an industrial tool or from a combination of industrial tool and firearm discharge. However, it may not be possible to distinguish the two possibilities.

Examination of the supporting particles is also useful in the determination of GSR negatives. If no unique particles are found during the initial search of the sample, yet characteristic or consistent particles are observed, the analyst may be encouraged to repeat the search over a different area, a larger area, at higher magnification, or lower backscatter detector threshold, etc., in an attempt to locate any unique particles that may have been missed. On the other hand, if no unique or supporting particles are found on the initial search, the analyst will have greater confidence that no GSR is present in the sample.

Examination of the non-unique particles may result in the identification of populations worth further investigation. This is particularly the case in samples from shootings involving unusual ammunition: tracer, armor piercing and other specialty types; or ammunition having lead free primers.

FORMATION OF GSR PARTICLES

Gunshot residue is formed principally by the condensation of vaporized primer and bullet materials either in the firearm itself or while in flight shortly after ejection from the muzzle, barrel/cylinder gap, ejection port, etc. (Tassa and Zeldes 1979; Wolten and Nesbitt 1980; Basu 1982). The particles most relevant to GSR analysis are derived from the primer. Modern priming mixtures for conventional nonmecuric noncorrosive ammunition contain the lead, antimony and barium salts which burn to produce particles with the characteristic GSR signature. Primers of this type have dominated the commercial market since the 1950's. Ammunition companies are generally secretive about their priming mixes, but most conventional formulations contain lead styphnate, barium nitrate, antimony sulphide, calcium silicide and tetracene. Numerous variations are reported in the literature, many of which specify additional components such as ground glass, aluminum, titanium, zirconium, other lead salts and organic compounds (Bydal 1990; Wallace 1990).

Wolten *et al.* (1979abc) discuss GSR in terms of two major populations: primer particles and bullet particles. Primer particles condense from vapors produced by the combustion of the priming mixture and consist mainly of oxides, sulphides and related oxy-salts of lead, antimony and barium (see Figure 1). Bullet particles are created from vapors produced by frictional heating of the projectile in the barrel and by erosion of the projectile by hot propellant gasses. They are mixtures of free metals, typically lead, antimony (hardened bullets and shot), and copper (jacketed bullets, plated bullets and shot). The appearance of copper in primer particles is accounted for by the oxidation of a portion of the bullet jacket or plating, which then readily mixes with the primer combustion products.

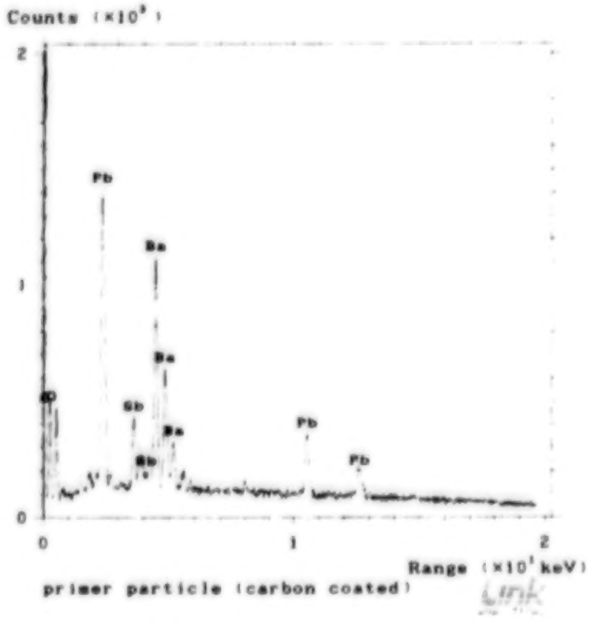


Figure 1. Thin window spectrum of a primer particle showing the lead, antimony and barium accompanied by oxygen.

Investigations into the structures of lead, antimony and barium particles by Basu (1982) gives further details on the mechanism of GSR formation. Particles begin as liquid droplets condensed during the supersaturated conditions following primer combustion but before propellant ignition. The droplets, containing varying amounts of lead, antimony and barium, grow by coalescence but eventually freeze, leaving a record of morphology and composition representative of the process of accreation the individual particle underwent. Smaller particles, generally less than 10µm in diameter, may form directly from the condensing vapors or by the fusion of other droplets, remaining liquid sufficiently long to mix uniformly. They are often homogenous in composition and represent the regular, irregular and nodular spheroids commonly seen in casework. Larger particles usually have a composition which is irregular and discontinuous, and have internal voids and surfaces with holes. They are formed by the fusion of multiple droplets where the particle has solidified before significant mixing occurred (see Figures 2 and 3). These particles comprise the atypical irregular shape and hollow sphere GSR seen occasionally. Larger particles may also have the so called "peeled orange" morphology which typically has a nucleus of barium and antimony partially covered by a layer of lead. Basu postulates that the lead layer is from bullet vapor condensing on a solid or solidifying barium-antimony core.

The proposed mechanisms account for the variability in shape and composition of GSR particles and suggest that the variability itself may be a feature that distinguishes GSR populations from environmental and occupational particles.

SAMPLING

Sampling is usually effected by adhesive lift (Ward 1982), followed in some laboratories by a concentration technique (Sugarman 1987; Zeichner *et al.* 1989). Other methods include the use of swabs and vacuum suction.

For adhesive lift sampling, the tape or glue is usually mounted on an aluminum or carbon SEM stub or similar rigid mount. The sample is taken by repeatedly placing the stub on the hand or face of the subject and lifting any particles present on the skin until the stickiness of the adhesive is lost. The area of skin sampled and the exact construction of the sample stub varies from laboratory to laboratory. Stubs of 1.3, 1.9 and 2.5 cm diameter are used, with compromises being made re-

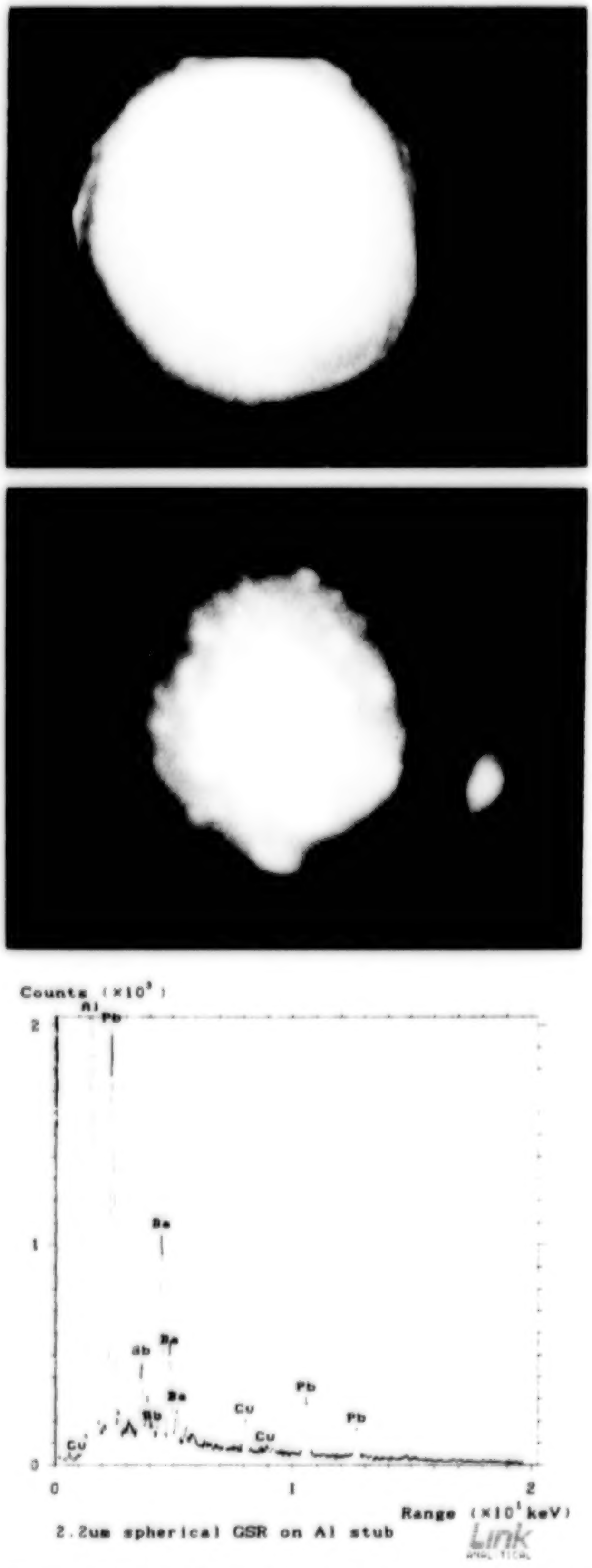


Figure 2. Spherical GSR particle. Figure 2a. Secondary electron image displaying the outer surface. Figure 2b. Backscatter electron image displaying the interior structure of fused particles. Figure 2c. EDX spectrum showing lead, antimony, barium and copper. The aluminum does not originate from the particle.

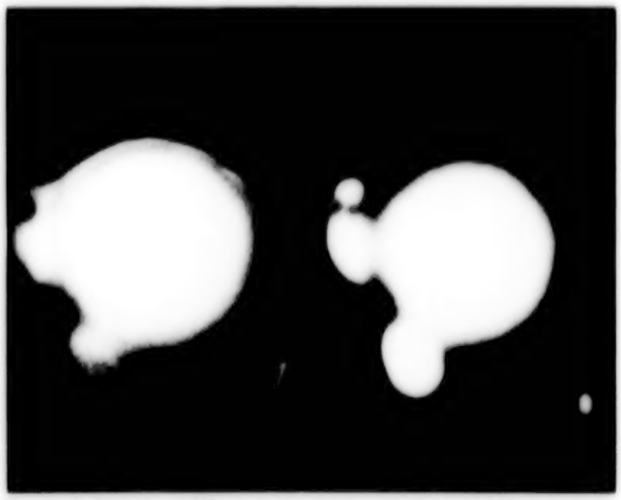


Figure 3. Nodular GSR particle composed of several homogenous droplets partially fused. Secondary electron image (left) and Backscatter image (right).

garding maximizing the adhesive area while keeping the stub small enough to fit the nooks and crannies of a hand or face. Some laboratories attach the adhesive to flexible plastic strips which allows the adhesive area to be arbitrarily increased without significantly affecting the ability to enter tight spaces.

The concentration technique begins with taking an adhesive lift sample. The glue is dissolved and the GSR particles are separated by density from the miscellaneous debris recovered from the skin. The GSR particles are removed by filtration and deposited onto a suitable substrate in an area less than five percent of the original. The concentration procedure significantly reduces the surface area necessary to be searched by SEM/EDX while still examining the bulk of the GSR in the original sample. Variations on the technique hold promise for collecting residues from places heavily contaminated by blood or other foreign material that would defeat an adhesive.

It is usually the hands of the suspected shooter that are sampled. Collecting from the face in addition to the hands offers some advantages. The face is subject to less abrasion than the hands and is less likely to be washed, so the lifetime of GSR particles on the face may be greater. Furthermore, the face is less likely to be covered by clothing. The face may be as close to the firearm as the hands at the time of discharge, particularly with rifles and shotguns. Most GSR kits used to sample hands can also be used to sample the face.

SAMPLE ANALYSIS

Analysis of the sample by SEM/EDX is commonly done using a manually controlled instrument (DeGaetano and Siegel 1990). The operator directly controls all aspects of the search and characterization of GSR particles. The manual method is adequate for low volume laboratories but is gradually being displaced by automated analysis in situations where the principal use of the instrument is GSR analysis. Automated instruments operate unattended overnight and on weekends, maximizing sample throughput.

In manual analysis, the sample is divided into an arbitrary grid such that each cell represents a normal field of view at the selected search magnification, typically 500X. The cells are searched one by one for particles of interest. The procedure is made practical by employing the backscatter electron detector. Features containing heavy elements like the lead, antimony and barium of GSR are brighter in the backscatter electron image and are easy to find (see Figure 4). Potential GSR particles are inspected at high magnification for correct morphology using the normal (secondary electron) imaging mode of the SEM. Finally, the electron beam is directed onto the particle and an x-ray spectrum is collected using the EDX. A record is made of the particle morphology and composition. The search ceases when sufficient GSR particles are located, or if negative, when a representative portion of the sample has been examined (Owens 1990).

Setup of the backscatter detector is critical for minimizing the risk of missing a GSR particle while simultaneously eliminating from view the unrelated light element particles. The lead, antimony and barium primer particles, being oxides and sulphides, have a much lower average atomic number than the metallic lead bullet particles and consequently have a lower backscatter brightness (see Figure 5). This contributes to the difficulty of finding them. A typical practice is to adjust the backscatter detector to show all micron sized particles heavier than iron.

Figure 4. Gunshot residue particle appearance in the secondary electron image (left) and backscatter electron image (right). The particles can easily be located in the secondary electron image using the backscatter image as a key.

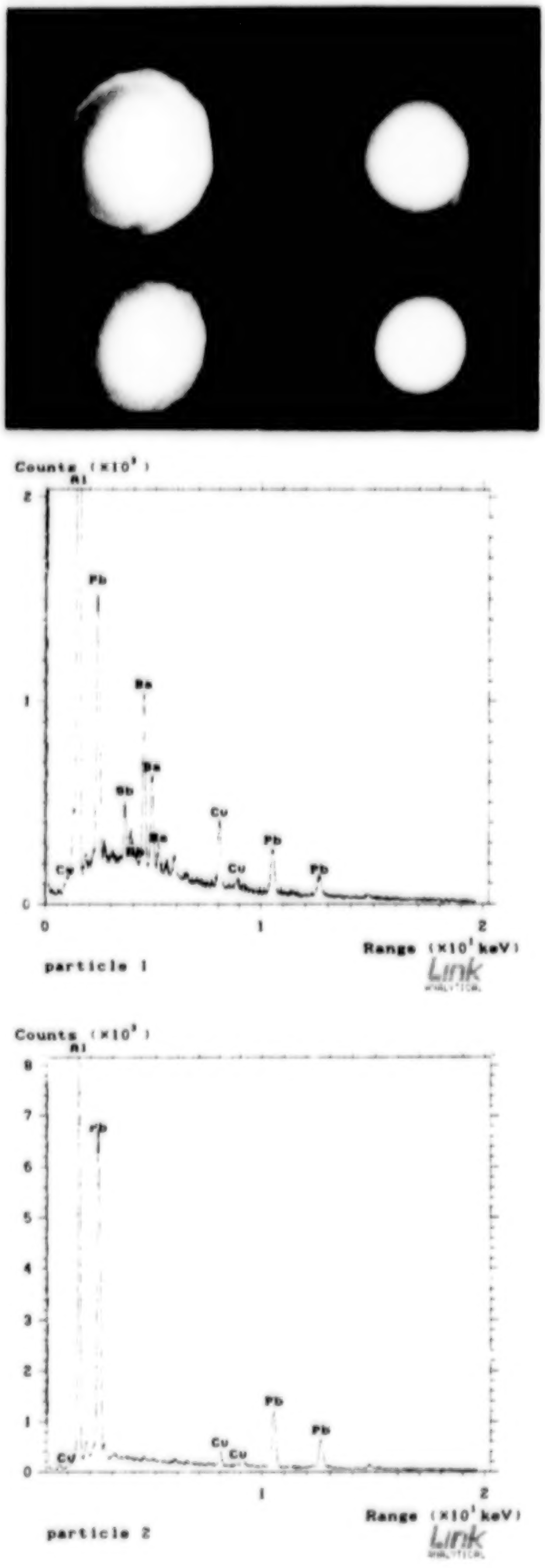
GSR particles, once found, are generally easy to analyze with the EDX. The main difficulty is dealing with spectral overlap between lead-sulphur-molybdenum, barium- titanium and antimony-calcium-tin. Some laboratories employ a WDX spectrometer, which has considerably better resolution than EDX, to resolve overlapped spectra (see Figure 6).

Operator boredom and fatigue is a major concern with the manual method. Samples may require several hours to a full day to search. This creates pressure to reduce the search area, particularly in negative cases. Insufficient sample may be searched to guarantee a true negative. On the other hand, the operator sees the morphology and composition of the entire population of backscatter bright particles.

Automated analysis is the answer to operator fatigue (Tillman 1987; White and Owens 1987; Germani 1991). The instrument performs essentially the same sequence of operations as would a human operator and can be left to analyze multiple samples overnight. The instrument controls a motorized stage to search a grid either sequentially or following a specified pattern, usually covering a substantial fraction of the sample surface. It searches the backscatter electron image of each cell for regions that exceed a specified video brightness. Although the grey level discrimination of the instrument is greater than that of the eye, the backscatter electron signal must be very stable over time. Otherwise the instrument will either miss all the particles and detect nothing, or become bogged down attempting to analyze every speck in the sample. The backscatter bright regions are analyzed automatically by the EDX (or WDX) and classified according to their composition. The classification process must be made sufficiently accurate to compensate for the operator not seeing the entire particle population as in the case of manual analysis. Upon completion of the automated analysis, typically taking less than five hours per sample, the operator can return to the particles of interest relatively quickly and manually confirm their classification and inspect morphology.

INTERPRETATION OF RESULTS

There are two aspects to the interpretation of particle data: the analytical result and its forensic significance. Both ought to be reported for the sake of accuracy and completeness. The analytical result deals with the assessment of the particle population and whether or not it constitutes GSR. The forensic significance concerns what the presence or absence of GSR means in the context of the case at hand. The scope and detail of written opinions will vary with the circumstances of the



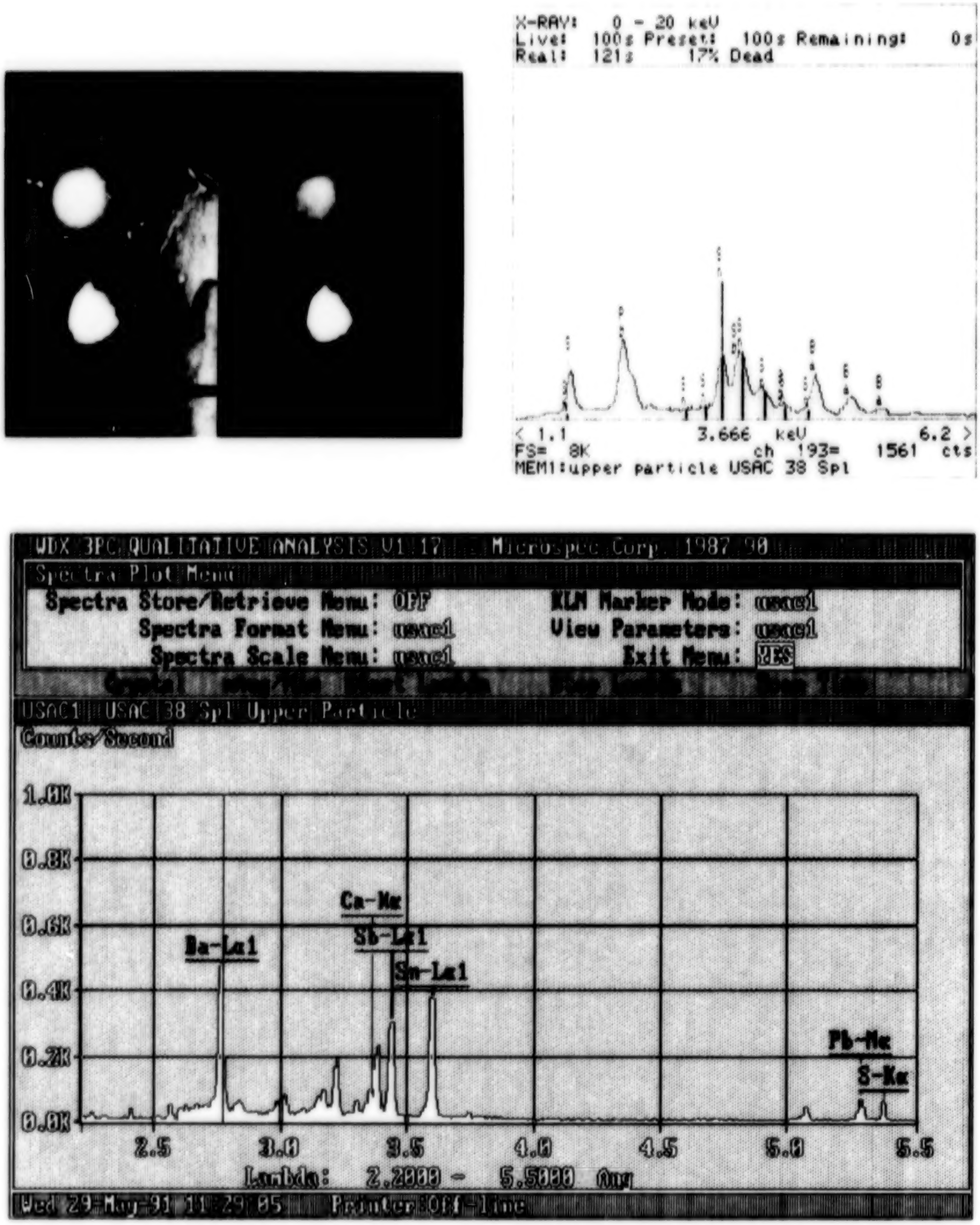
case and the nature of the legal system in which the analyst operates.

Establishing the presence of GSR from conventional ammunition is well documented and generally refers to ammunition of all types that contains primers having conventional percussion mixes. Since the only known source of unique particles is GSR, finding at least one such particle means that GSR has been detected. The presence of unique particles cannot be ignored until some arbitrary number are located. However, examination of the remaining population may lead to the conclusion that the residue is potentially from a cartridge powered industrial tool or some other non-firearm. Determination of a GSR negative is less definitive. Unless every square millimeter of the sample surface is searched under instrumental conditions where it would be nearly impossible to miss a GSR particle, which is rarely if ever achieved, then one cannot draw the conclusion that there is no GSR present in the sample. Analysts typically sidestep the issue by reporting that no GSR was detected, or if sufficient sample area was searched, that the sample probably does not contain GSR.

The 22 rimfire calibers pose additional problems as their primers often do not contain all three signature elements (Meyers and Kopec 1976). Since antimony is usually the missing component, only the barium-calcium-silicon unique combinations are possible, and suspicion has been cast on their usefulness. Some 22 caliber priming mixtures contain neither antimony nor barium. The only hope in such a situation is that carry over of residue present from a previous firing of a different brand of ammunition may contain the signature elements.

The use of unusual or specialty ammunition creates more difficulty for the analyst, particularly if the priming mixture does not contain conventional compounds. Ammunition which has conventional priming in combination with unusual elements in the primer or elsewhere is easier to deal with, since the allowed list of elements can be expanded to reflect the additions. For example, USA Co. ammunition has a tin plated aluminum cartridge head. The tin is widely distributed through the particle population. Tracer ammunition often has magnesium and strontium in the bullet. Some East European and obsolete North American ammunition has primers based on mercuric fulminate. The new lead free primed ammunition for indoor range practice may not contain any of the conventional signature elements. Dynamit

Figure 5. Two homogenous composition GSR particles. Figure 5a. Secondary electron image (left) and backscatter electron image (right). The bottom particle, being mostly lead, has a higher average atomic number and consequent brighter backscatter image. Figure 5b. EDX spectrum for the upper particle showing unique composition. Figure 5c. EDX spectrum for the lower particle showing characteristic composition. the aluminum does not originate from either particle.



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X-RAY:    0 - 20 keV
Live:   100s Preset:   100s Remaining:     0s
Real:   121s      17% Dead
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FS=  8K               ch  193=    1561  cts
MEM1:upper particle USAC 38 Spl
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WDX 3PC QUALITATIVE ANALYSIS V1.17 . Microspec Corp. 1987 90

Spectra Plot Menu

Spectra Store/Retrieve Menu: OFF

Spectra Format Menu: usac1

Spectra Scale Menu: usac1

KLM Marker Mode: usac1

View Parameters: usac1

Exit Menu: YES

USAC1 USAC 38 Spl Upper Particle

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Figure 6. GSR particles form test firing USAC 38 Special caliber ammunition. Figure 6a. Secondary electron image (left) and backscatter electron image (right). The upper particle contains lead, antimony, barium and tin, while the lower particle has lead, antimony and tin only. Figure 6b. EDX spectrum for the upper particle. The lead, barium and tin are clearly depicted. The presence of antimony is suggested by the broadening of the tin lines. Figure 6c. WDX spectrum for the same particle clearly separates the tin and antimony peaks. it also shows the presence of calcium and sulphur which were hidden under the antimony/tin and lead lines respectively.

Nobel Sintox primers are reported (Wallace 1990) to be based on zinc and titanium compounds. Populations of particles containing unusual elements can be compared to those of test samples made using ammunition recovered in connection with the shooting. However, it is unknown whether any of the non- conventional primer particles can be construed as unique.

Samples from a suspected shooter's hands or face are usually taken in connection with homicides, assaults and the like, or for suicide verification (Reed *et al.* 1990). Many laboratories do not analyze samples from suicide victims, often due to a more general policy of not accepting samples from close range shooting victims. They are presumed to have been sufficiently close to the muzzle of the firearm to have GSR deposited almost anywhere on the body (Thornton 1986). In the case of suicides, only a negative result would normally be significant, especially without a suitable explanation for the absence of GSR (22 rimfire caliber ammunition, body putrefied, etc.).

In the case of criminal shootings the question usually posed by the police investigator is whether or not the suspect discharged a firearm recently. The residues from firearms typically are deposited on surfaces up to six feet distant, depending on the type and calibre of the firearm and ammunition. The shooter or anyone else within that radius can have GSR driven onto their hands and face. If GSR is detected during analysis, the conclusion normally drawn is that the person whose hands (or face) were sampled recently discharged a firearm, was near a firearm being discharged or was in contact with a firearm or similar source of gunshot residue. The emphasis given to the final category, incidental contamination, can vary considerably depending on the circumstances of the case. On the other hand, a negative result for GSR cannot be taken to mean that the subject has not recently fired a firearm.

The lifetime of GSR on live subjects is variously reported in the literature as being from two to twelve hours. This is both a blessing and a burden. The culprit must be sampled within the time limit to collect GSR. However if residue is detected, then it must have been acquired recently, not during last week's or last year's hunting trip.

SUMMARY

Particle analysis by SEM/EDX is an ideal method of analysis of GSR and particularly suited to the needs of the criminal courts, being definitive for GSR. Although it is still feasible to perform the analysis on a manual instrument, recent advances in automation have greatly increased sample throughput and made the method practical.

ACKNOWLEDGEMENTS

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REFERENCES

Andrasko, J. and Maehly, A. C. (1977). Detection of gunshot residues on hands by scanning electron microscopy, J. Foren. Sci. 22:279-287.

Basu, S. (1982). Formation of gunshot residues, J. Foren. Sci. 27:72-91.

Bydal, B. A. (1990). Percussion primer mixes, Assoc. Firearms Toolmark Examiners J. 22:1-26.

DeGaetano, D. and Siegel, J. A. (1990). Survey of gunshot residue analysis in forensic science laboratories, J. Foren. Sci. 35:1087-1095.

Germani, M. S. (1991). Evaluation of instrumental parameters for automated scanning electron microscopy/gunshot residue particle analysis, J. Foren. Sci. 36:331-342.

Meyers, R. E. and Kopec, R. J. (1976). Identification of .22 calibre rimfire ammunition suitable for gunshot residue determination, Identification News, Sept. 10-13.

Owens, A. D. (1990). A re-evaluation of the aerospace corporation final report on particle analysis - when to stop searching for gunshot residue (GSR)?, J. Foren. Sci. 35:698-705.

Reed, G. E., McGuire, P. J. and Boehm, A. (1990). Analysis of gunshot residue test results in 112 suicides, J. Foren. Sci. 35:62-68.

Sugarman, L. A. (1987). The concentration and isolation of gunshot residues for particle analysis, Presented at the 39th Annual Meeting of Am. Acad. Foren. Sci., San Diego, California, Feb.

Tassa, M. and Zeldes, N. (1979). Characterization of gunshot residue particles by localizations of their chemical constituents, Scanning Electron Microscopy II:175-178.

Thornton, J. I. (1986). Close proximity gunshot residues, J. Foren. Sci. 31:756-757.

Tillman, W. L. (1987). Automated gunshot residue particle search and characterization, J. Foren. Sci. 32:62-71.

Wallace, J. S. (1986). Discharge residue particles from blank cartridges, Assoc. Firearms Toolmark Examiners J. 18:33-39.

Wallace, J. (1990). Chemical aspects of firearms ammunition, Assoc. Firearms Toolmark Examiners J. 22:364-389.

Wallace, J. S. and McQuillan, J. (1984). Discharge residues from cartridge-operated industrial tools, J. Foren. Sci. Soc. 24:495-508.

Ward, D. C. (1982). Gunshot residue collection for scanning electron microscopy, Scanning Electron Microscopy III:1031-1036.

White, R. S. and Owens, A. D. (1987). Automation of gunshot residue detection and analysis by scanning electron microscopy/energy dispersive x-ray analysis (SEM/EDX), J. Foren. Sci. 32:321-330.

Wolten, G. M. and Nesbitt, R. S. (1980). On the mechanism of gunshot residue particle formation, J. Foren. Sci. 25:533-545.

Wolten, G. M., Nesbitt, R. S., Calloway, A. R., Loper, G. L. and Jones, P. F. (1977). Final report on particle analysis for gunshot residue detection, Report ATR-77 (7915)- 3, Aerospace Corporation, El Segundo, CA, Sept.

Wolten, G. M., Nesbitt, R. S., Calloway, A. R., Loper, G. L. and Jones, P. F. (1978). Final report on particle analysis for gunshot residue detection", Report ATR-77 (7915)-3 Addenda and Errata, Aerospace Corporation, El Segundo, CA, May.

Wolten, G. M., Nesbitt, R. S., Calloway, A. R., Loper, G. L. and Jones, P. F. (1979a). Particle analysis for the detection of gunshot residue. I: Scanning electron microscopy/energy dispersive X-ray characterization of hand deposits from firing, J. Foren. Sci. 24:409-422.

Wolten, G. M., Nesbitt, R. S., Calloway, A. R. and Loper, G. L. (1979b). Particle analysis for the detection of gunshot residue. II: Occupational and environmental particles, J. Foren. Sci. 24:423-430.

Wolten, G. M., Nesbitt, R. S. and Calloway, A. R. (1979c). Particle analysis for the detection of gunshot residue. III: The case record, J. Foren. Sci. 24:864-869.

Zeichner, A., Foner, H. A., Dvorachek, M., Bergman, P. and Levin, N. (1989). Concentration techniques for the detection of gunshot residues by scanning electron microscopy/energy dispersive x-ray analysis (SEM/EDX), J. Foren. Sci. 34:312-320.

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AN OVERVIEW:
ATOMIC ABSORPTION SPECTROPHOTOMETRY IN FORENSIC SCIENCE

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Donelson, Tennessee

Modern Atomic Absorption Spectrophotometry (AAS) has its roots in the early part of the eighteenth century scientists with such as Wollaston, Brewster, Kirchoff, and Bunson (Rubeska and Moldan 1967). These scientists were investigating the sun in an effort to determine the composition of it's light and atmosphere. In doing so they and others laid down the foundations of spectrochemical analysis. Their work cannot be understated and it is well worth noting that the phenomenon of line spectra and their production is still not well explained.

Out of this work emerged the relationship between emission spectra and absorption spectra. According to Kirchoff's Law: "ALL MATTER ABSORBS LIGHT AT THE WAVELENGTH AT WHICH IT EMITS" Later Planck established the quantum law of absorption and emission of radiation. According to this law an atom can only take up and release unit amounts of energy at specific wavelengths (Figure 1).

These are the principles which outline the application of AAS in chemical analysis. The practical significance of these principles was not recognized for quite some time. Some of the delay could well have stemmed from the fact that high quality optics were not commercially available until about 1925. Even then the technique of choice was emission spectroscopy, not AAS.

Modern AAS started in the mid 1950's with reports from Walsh, Alkemade and Milatz (Waltz 1985). It was the Australian physicist, Walsh who patented his equipment, and aggressively sought to interest instrument manufacturers in its production. He succeeded in 1962 with the Perkin-Elmer corporations. Since that time, the rapid development and refinement of his technique has been astonishing. Figure 2 is a simplified instrument optic pathline.

The basic principals for AAS instrumentation have changed little since Walsh's spectrophotometer. However, there have been many improvements with regard to electronics, optics, automation, background correction and sample automation. As a result, AAS's sensitivity for analysis of metals is often regarded as being the technique of choice. Table 1 lists representative current sensitivities.

Commonly, instrument manufactures provide cookbook techniques for arriving at instrument specified sensitivities. This is always a good place to start method development for a particular analysis. Table 2 lists parameters for our particular AAS.

FORENSIC CONSIDERATIONS

As far as the forensic scientist is concerned, there are a number of specific issues which must be addressed before, during, and after an analysis. These questions must be answered to give an expert opinion as to what certain elemental levels mean:

- What elements are normally present in a sample?

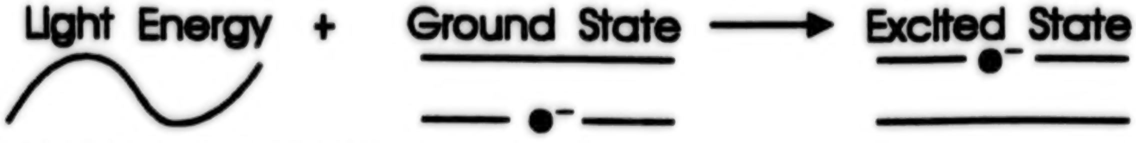

Figure 1. Energy released at specific wavelengths.

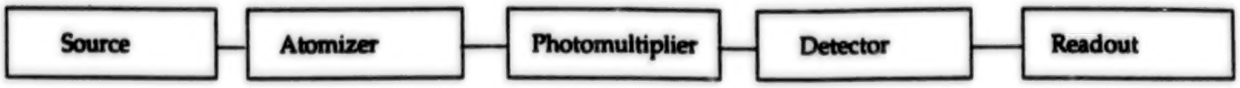

Figure 2. Simplified instrument optic for atomic absorption spectrometry.

- How much is normally present?
- Can the elements in question be attributed to a specific activity?
- What is the distribution of these elements?
- Can any correlations be made in these distributions?
- Is AAS the method of choice?

GUNSHOT PRIMER RESIDUE

The ability to determine whether an individual has recently fired a weapon has long been of interest to forensic laboratories because of its obvious value in criminal investigations. I believe AAS can often provide answers but they are seldom the exact answers that everyone wants to hear.

Table 1. ATOMIC ABSORPTION SPECTROMETRY SENSITIVITY FOR ANALYSIS OF METALS

ELEMENT	FURNACE (100µl sample)	FLAME
Ag	0.005	1
Al	0.01	30
As	0.2	20
Au	0.1	6
B	15	1000
Ba	0.04	10
Be	0.03	2
Bi	0.1	1
Ca	0.05	1
Cd	0.003	6
Co	0.02	6
Cr	0.01	2
Cu	0.02	1
Fe	0.02	5
Hg	2	200
K	0.002	1
Li	0.2	0.5
Mg	0.004	0.1
Mn	0.01	1
Mo	0.02	30
Na	0.01	0.2
Ni	0.2	4
P	30	50000
Pb	0.05	10
Pt	0.2	40
Sb	0.1	30
Se	0.5	100
Si	0.1	50
Sn	0.1	20
Te	0.1	20
Ti	0.5	50
V	0.2	40
Zn	0.001	1

These limits are determined by the noise level and signal output.
Reported as µg/l.
Courtesy Perkin-Elmer Corporation.

In order to have a better understanding of Gunshot Primer Residue (GSR) a brief examination of the history of firearms munitions is in order. Black powder and its difficulty in safe ignition has long been known to man (Bartlett and Gallatin 1956). The first ignition systems in handheld firearms usually consisted of a burning cord. This cord was soaked in potassium nitrate solution and burned slowly. A number of ingenious mechanical devices followed for the introduction of a spark into the powder (Blackmore 1965; Hoggs 1978) and is depicted in Figure 3.

The popular use of a chemical formulation to initiate a discharge is generally attributed to Alexander Forsyth in 1807. This Scottish clergy - man used mercury fulminate {$Hg(ONC)_2$} in his design of a fowling piece. This brought about the ignition system known as percussion which dominated firearms of the eighteenth century. These firearms are still in production today as hunting and enthusiast weapons. The general principle of striking a contained primer composition to initiate discharge is still the basis of modern firearm ammunition construction.

During the American Civil War the self contained metallic cartridge case was developed (Hunt 1987). Following the Civil War these cartridge cases evolved very rapidly mainly due to the development of the Boxer and Berdan primers (Klatt 1972). The metallic cartridge case is still used in modern ammunition, although the primer and propellant components are markedly different from those first cartridges. Figure 4 illustrates modern systems of ignition.

Black powder as the principal propellant in ammunition was phased out by the turn of the century (Dutton 1942). The invention and ultimate safe production of nitrocellulose based powders caused a great deal of design changes in weaponry (Longridge 1890). During this time it became evident that a number of problems had to be solved. First, the free mercury generated from the primer did not absorb into the new smokeless powder residues. Instead, it amalgamated with the zinc in the brass of the cartridge cases, making the cases brittle and unsafe for reloading. Eventually mercury was found to be a health hazard, so efforts to replace it had a second motivation.

The next generation of primer compositions generally contained potassium chlorate, sulfur, antimony sulfate and often glass dust. However, the shelf life of some variations of these primers was short due to impurities associated with the potassium chlorate and the sulfur. Additionally, all primer compositions which contained potassium chlorate left corrosive residues in the barrels of weapons which greatly shortened the life span of the weapon.

Finally, a composition that was mercury free and noncorrosive was produced with eventual wide accep-

Table 2. ATOMIC ABSORPTION SPECTROMETRY INSTRUMENT PARAMETERS

Element	λ	Slit	P/W	Modifier	Pretreat	Atom.	Mo	Check	Roll
Ag	328.1	0.7	P	0.2 mg PO_4	650	1600	1.4	3.2	1.8
Al	309.3	0.7	P	0.05 mg Mg $(NO_3)_2$	1700	2500	10.0	22.7	0.8
As	193.7	0.7	P	0.02 mg Ni	1300	2300	17.0	38.6	1.3
Au	242.8	0.7	P	0.05 mg Ni	1000	2200	13.0	29.5	1.6
B	249.7	0.7	W	0.005 mg Ca	1000	2650	1000.0	2270.0	0.5
Ba	553.6	0.2	W		1200	2650	6.5	14.8	1.8
Be	234.9	0.7	P	0.05 mg Mg $(NO_3)_2$	1500	2500	1.0	2.3	0.5
Bi	223.1	0.2	P	0.02 mg Ni	900	1900	24.0	54.5	1.8
Ca	422.7	0.7	W		1100	2600	0.8	1.8	1.8
Cd	228.8	0.7	P	0.2 mg Po_4 + 0.01 mg $Mg(NO_3)_2$	900	1600	0.35	0.8	0.8
Co	242.5	0.2	P	0.05 mg Mg $(NO_3)_2$	1400	2500	7.0	15.9	1.0
Cr	357.9	0.7	P	0.05 mg Mg $(NO_3)_2$	1650	2500	3.3	7.5	1.6
Cs	852.1	0.7	P	0.2% H_2So_4	900	1900	5.3	12.0	1.8
Cu	324.8	0.7	P		1000	2300	8.0	18.2	0.7
Dy	421.2	0.2	W		1500	2650	40.0 *	90.9 *	
Er	400.8	0.2	W		1700	2650	70.0 *	159.0 *	
Eu	459.4	0.2	W		1300	2600	20.0 *	45.4 *	
Fe	248.3	0.2	P	0.05 mg Mg $(No_3)_2$	1400	2400	5.0	11.4	0.8
Ga	287.4	0.7	W		800	2650	52.0 *	118.0	1.3
Gd	407.9	0.2	W		1600	2650	11000.0 *	25000.0 *	
Ge	265.1	0.2	P	0.05 mg Mg $(No_3)_2$	950	2400	34.0	77.3	1.8
Hg	253.7	0.7	W **	10 mg Te in 1% HC	150	2000	210.0 *	477.0 *	0.3
In	325.6	0.7	P		800	1400	12.0	27.3	1.2
Ir	264.0	0.2	W		1300	2650	250.0	568.0	1.0
K	766.5	0.7	W		950	1500	1.1 *	2.5	1.8
La	550.0	0.2 †	W		1600	2650	26400.0 *	60000.0 *	
Li	670.8	0.2 †	P		900	2600	1.4	3.2	1.8
Mg	285.2	0.7	P		900	1700	0.35	0.80	1.0
Mn	279.5	0.2	P	0.05 mg Mg $(No_3)_2$	1400	2200	2.2	5.0	1.1
Mo	313.3	0.7	W		1800	2650	9.0	20.5	1.8
Na	589.0	0.7 ††	W		900	1500	1.0 *	2.3 *	1.8
Nd	463.4	0.2 †	W		1500	2650	1800.0 *	4090.0 *	
Ni	232.0	0.2	P		1400	2500	13.0	29.5	0.7
Os	290.9	0.2	W		200	2650	1400.0 *	3180.0 *	
P	213.6	0.7	P	0.05 mg La $(No_3)_2$	1400	2650	3000.0	6820.0	0.7
Pb	283.3	0.7	P	0.2 mg PO_4 + 0.01 mg Mg $(NO_3)_2$	900	1800	12.0	27.3	1.5
Pd	247.6	0.7	P		900	2650	24.0	54.5	1.3
Pt	265.9	0.7	W		1300	2650	115.0 *	261.0 *	1.1
Rb	780.0	0.7 ††	P		800	1900	2.4	5.4	1.8
Rh	343.5	0.2	W		1300	2400	12.0 *	27.3 *	
Ru	349.9	0.2	W		1400	2500	36.0 *	81.8 *	1.4
Sb	217.6	0.7	P	0.02 mg Ni	1100	2400	38.0	86.4	1.4
Se	196.0	2.0	P	0.02 mg Ni + 0.025 mg Mg $(NO_3)_2$	900	2100	30.0	68.2	1.4
Si	251.6	0.2	P		1400	2650	40.0	90.9	1.8
Sm	429.7	0.2	W		1400	2600	240.0 *	545.0 *	
Sn	286.3	0.7	P	0.2 mg PO_4 + 0.01 mg Mg $(NO_3)_2$	800	2100	23.0	52.3	1.8
Sr	460.7	0.7 ††	W		1300	2600	1.4	3.2	1.8

Continued on Page

Table 2. ATOMIC ABSORPTION SPECTROMETRY INSTRUMENT PARAMETERS — Continued

Element	λ	Slit	P/W	Modifier	Pretreat	Atom.	Mo	Check	Roll
Te	214.3	0.2	P	0.02 mg Ni	1000	2000	15.0	34.1	1.1
Ti	354.3	0.2	W		1400	2650	43.0	97.7	1.8
Tl	276.8	0.7	P	1% H_2SO_4	600	1400	17.0	38.6	0.6
Tm	371.8	0.2	W		1700	2650	13.0*	29.5*	
U	351.5	0.2	W		1000	2650	12000.0*	27300.0*	
V	318.4	0.7	W	0.05 mg Mg $(NO_3)_2$	1100	2650	40.0	90.9	1.3
Y	410.2	0.2	W		1400	2650	13000.0*	29500.0*	
Tb	308.8	0.2	W		1300	2500	2.5*	5.7*	
Zn	213.9	0.7	P	0.006 mg Mg $(NO_3)_2$	700	1800	0.1	0.23	1.0

Data in Absorbance (peak height). ** Uncoated tube and normal heating
0.4 on a z/5000 †† 1.4 on aZ/5000 Courtesy Perkin-Elmer Corporation

tance (Bydal 1990). These compositions are based on the SINOXID patents containing tetracene as a sensitizer, antimony sulfide and calcium silicate, as fuels, and lead styphanate as the explosive. There have been and will continue to be variations of primer compounds, but most resemble one of the SINOXID patents.

Currently, there are some new compositions being marketed as lead free and at least one which is antimony, barium and lead free (Meyer 1987; Kass, personal communication). Whether these represent another generation or merely curiosities remains to be seen. Table 3 lists primer compositions. Figure 4 shows current configurations of primers.

GSR TECHNIQUES

The first efforts to determine if a subject recently fired a weapon centered around the residues from the nitrocellulose propellant which deposited on the hands of a shooter. In 1922, Benitez recommended the application of diphenylamine reagent to the interior of a paraffin mold of the hands (Benitez 1922). This test remained

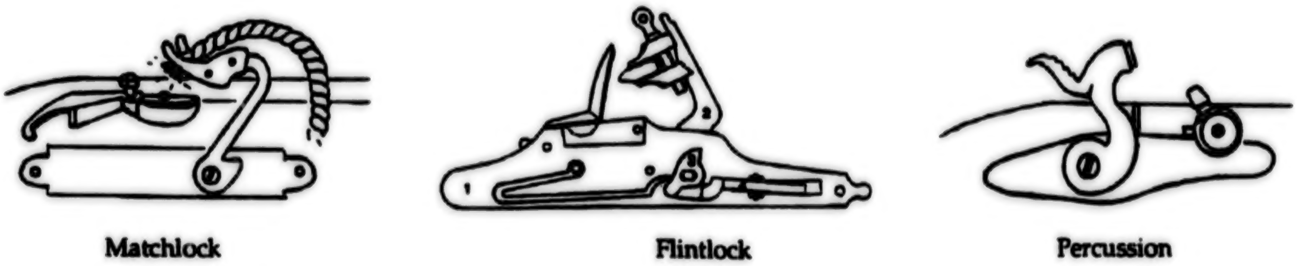

Figure 3. Illustration of mechanical devices for introducing spark into powder.

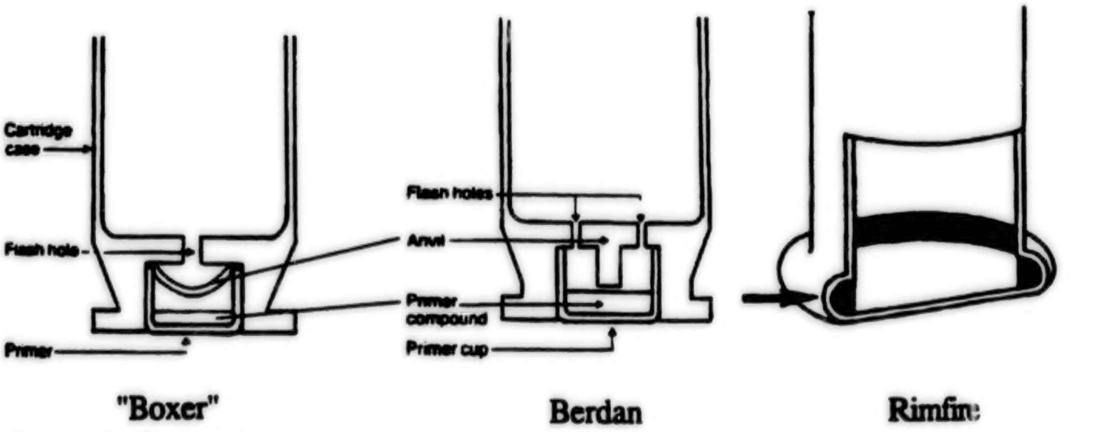

Figure 4. Modern systems of ignition of powder.

Table 3. PRIMER COMPOSITION GENERATIONS

ONE (1807 - 1900)

MERCURY FULMINATE

TWO (1900 - 1956)

POTASSIUM CHLORATE
LEAD THIOCYANATE
ANTIMONY SULFIDE
SULFUR
TNT
GUM ARABIC

THREE (1920 - PRESENT)

ANTIMONY SULFIDE
BARIUM NITRATE
LEAD STYPHINATE
TETRAZENE
CALCIUM SILICATE
LEAD DIOXIDE
GLASS POWDER

FOUR (LATE 1980's)

DIAZODINITROPHENOL
STRONTIUM DIAZODINITRORESORCINATE
ZINC PEROXIDE
TETRAZINE
TITANIUM POWDER

for a number of years even though it was pointed out time and time again that the reagent also reacted in the same manner with many common residues found on the hands of nonshooters (FBI 1935, 1940; Cowan and Purdon 1967). Today, the paraffin test has been totally discredited and serves as an example of a technique which saw legal acceptance far too long.

A number of attempts have been made to determine if an individual has recently fired a gun (Dahl *et al.* 1967). In the early 1960's the Gulf Atomic Group demonstrated that Neutron Activation Analysis (NAA) was an excellent method for measuring elements found on the hands of shooters and non-shooters (Buchanan and Ruch 1964; Colman 1967). This technique has the singular shortfall of needing access to a nuclear reactor. NAA is still in use today (Kilty 1986).

Currently AAS is one of two main methods of analysis for GSR (DeGaetano 1986). With improved atomization techniques, improvement in sensitivities, and lower cost, the potential for GSR analysis was realized (Goleb and Midkiff 1975; Renshaw 1973; Renshaw *et al.* 1973; Cone 1973). The technique has been refined over the last seventeen years into a fairly standardized analysis (Koons *et al.* 1987, 1989; Wallace 1987; Newton 1981; Newbury 1980).

When a weapon fires a number of events occur in a matter of milliseconds after the primer is struck. First, the primer composition is crushed with resulting ignition of the mixture. Hot debris and flame spew forward to the propellant which then ignites and burns rapidly. This produces a large volume of gases under very high pressure which forces the projectile(s) out of the cartridge case and down the barrel (Scott, personal communication). As this happens the gases vent out of the barrel, cylinder gap or ejection port. These gasses then rapidly cool and deposit on any nearby surface.

A number of factors come into play to affect the success of collection of these residues:

- Collection technique
- Time interval from shooting till collection
- Activity of/on the surface to be collected
- Ammunition
- Weapon

There have been several efforts to optimize the collection of GSR (Goleb and Midkiff 1974; Pillay *et al.* 1974; Krishnan 1982; Green and Savve 1972). Cotton tipped, plastic shafted swabs moistened with a few drops of 5% nitric acid is generally the most used technique and dominate the commercially available kits.

The typical procedure for collection of GSR is to moisten a swab with a few drops of 5% nitric acid solution and thoroughly wipe each surface of both hands. Our laboratory has demonstrated that two swabbings should be performed as one is insufficient for complete removal of residues. These are separately packaged along with a moistened control swab.

The fact that GSR is easily removed from a shooter's hands has been demonstrated a number of times (Kilty 1975; Krishnan 1972; Rudzitis 1980). Since the GSR is only on the surface of the hands, it easily rubbed or washed off. Therefore it is very important to swab the subject's hands as quickly as possible. It follows that if a weapon is clean and of tight construction, little residue will be emitted. Additionally, handguns discharge GSR in the immediate vicinity of the firing hand. Shotguns and rifles seem to emit GSR primarily from the end of the barrel, in the immediate vicinity of the non-shooting or support hand.

Currently, a number of brands of .22 ammunition do not have in their primer composition all the elements needed for GSR determination. Remington has only lead compounds, CCI and Winchester-Western have only barium and lead. CCI has recently been marketed 9 mm as lead free, and factory reload brand 3-D markets 9 mm and .38 which are lead free. Reportedly, PMC uses primers which are without antimony. GICO currently is marketing 9 mm ammunition with SINTOX primers which are antimony, barium, and lead free. For this reason collection kits have provisions for swabbing the cartridge case.

Another source of useful information is a file of shooting standards using various ammunitions and firearms. These can show expected levels, and when used with timed activity, these can show expected rates at which GSR may be lost.

Additionally, the ratios of each of these elements to each other is insignificant (Koons, personal communication). Since the primer composition undergoes a chemical reaction, certain results are expected. This ratio for antimony and barium may be between 1:1 and 1:10. Our laboratory expects the barium to lead ratio to be at least 1:1. All three elements are present but many labs look only for antimony and barium. See Appendix A for GSR parameters.

OPINIONS

Since the particles have been dissolved for collection and analysis the definitive identification has been ruled out. Only elements consistent with GSR that were found can be reported, along with an opinion of whether a subject fired or handled a weapon. Likewise, in the absence of elements being found, the test cannot rule out the possibility of a subject having fired or handled a weapon. The possibility that the subject's hands were merely in an environment where GSR was produced is very real and must be included in a positive opinion.

GSR RELATED

AAS has also been used to investigate other areas of interest besides the hands. Distance determination has been investigated by several authors (Krishnan 1982; Villanueva *et al.* 1987). However, other procedures dominate this area (Carman, personal communication).

Bullet lead and shotgun pellets have also been scrutinized via AAS but another technique NAA dominates (Brunelle *et al.* 1970; Blacklock and Sadler 1978).

OTHER AREAS

One material which has seen a number of attempts at elemental analysis is glass (Ryland and Koons 1991; Pitts and Kratochvil 1991; Koons et al. 1988b; Ryland 1986; Hickman 1981, 1982; Coleman and Weston 1968; Dobbs et al. 1973; Smale 1973; Kilroy and Moynihan 1976). At this point in time AAS is not at the forefront of this research, but Ion-Coupled Plasma Emission Spectroscopy (ICP) is.

Any number of references to analysis of a particular material can be found in literature (Hoffman *et al.* 1969; Hausknect *et al.* 1982; Price 1972; Covick 1982; Crow and Connolly 1973; McKenzie 1980; Knight and Pyzyz 1969). The technique and instrumentation are well established, but the problems for forensic scientists are still in the interpretation of the data. Unfortunately, these problems with data do not appear to be under active investigation; therefore, other techniques are more appropriate.

POISONS

Increasing technological use of metals has served as a measure of man's progress. This use has posed hazards to our health from the time metals were made into spear points to present day exposures to space age metals, alloys, or salts. Natural exposure to metals probably first came from foods and water. Metals leached from cookware or eating utensils, increasing the risk of exposure. Intentional use of pesticides which contain compounds of toxic metals and therapeutic preparations further increased the opportunity for hazardous exposures.

Some metals are necessary for good health. Others have no known biological function and are not serious health hazards. Still other non-essential elements are toxic and can cause serious harm, disease, and even death.

Although excessive concentrations of metals may occur in the air, water, or soil, technological use of their nondegradable compounds has lead to their accumulation in our environment. Metals thus released may enter the food chain. Daily intake of some metals is shown in Table 3 (Hammond and Beliles 1982).

Metals in their elemental form rarely interact with biological systems. Rather, it is the compounds of metals which interact with cellular processes. Soluble salts of metals dissociate in the aqueous environment of cell membranes and are easily transported as ions. The varying ease of dissociation directly relates to the toxic potential of the parent compound. The metal based gasses tend to be the most dangerous, followed closely by water soluble salts, and somewhat less the organically bound metals. The metals having the greatest potential for causing damage accumulate in the body's tissues and organs and are not readily eliminated or excreted.

ARSENIC

In nature, arsenic is the twentieth most common element and can be found everywhere in the earth's crust in widely varying amounts. The natural forms are typically sulfide complexes and iron pyrites. Only rarely is it encountered in its elemental form. The average human intake is 0.5 to 1.0 mg daily. The highest concentrations in food are in fish and crustaceans with levels of 1.5 to 100 ppm being reported (Schroeder and Balassa 1986). After decades of pesticide and herbicide use, soil levels of several hundred ppm have been reported by Gorby (1988) and can be viewed in Table 4.

Currently industrial use of arsenic compounds are on the decline with a few exceptions. Modern antibiotics have eliminated the use of arsenic tonics for all human pharmaceuticals but have remained in some veterinary medicine preparations for parasite eliminations (Collier, personal communication). As seen in Table 5, hydrocarbon-based insecticides have replaced the arsenic based commercial solutions. Arsenic is still used in herbicides,

Table 4. BODY BURDEN AND HUMAN DAILY INTAKE AND CONTENT IN THE EARTH'S CRUST OF SELECTED ELEMENTS

ELEMENT	HUMAN BODY BURDEN (mg/70 kg)	DAILY INTAKE (mg)	EARTH'S CRUST (ppm)
Aluminum	100	36.4	81,300
Antimony	<90		0.2
Arsenic	<100	0.7	2
Barium	16	16	400
Boron	<10	0.01-0.02	16
Cadmium	30	0.018-0.20	0.2
Calcium	1,050,000		36,300
Cesium	<0.01		1
Chromium	<6	0.06	200
Cobalt	1	0.3	23
Copper	100	3.2	45
Germanium	Trace	1.5	1
Gold	<1		0.005
Iron	4,100	15	50,000
Lead	120	0.3	15
Lithium	Trace	2	30
Magnesium	20,000	500	20,900
Manganese	20	5	1,000
Mercury	Trace	0.02	0.5
Molybdenum	9	0.35	1
Nickel	<10	0.45	80
Niobium	100	0.60	24
Potassium	140,000		25,900
Rubidium	1,200	10	120
Selenium	15	0.05 - 0.15	0.09
Silver	<1		0.1
Sodium	105,000		28,300
Strontium	140	2	450
Tellurium	600	0.6	0.002
Tin	30	17	3
Titanium	<15	0.3	4,400
Uranium	0.02		2
Vanadium	30	2.5	110
Zinc	2,300	12	65
Zirconium	250	3.5	70

fungicides, and dips for cattle and sheep. One area which has seen an increase in demand for arsenic is the wood preservative industry. The principal demand for arsenic is as the oxide (As_2O_3) from manufacturers of various products (Figure 5).

Arsenic has long been synonymous with poison. Historically, arsenic has long been used as a poison. An early, well- documented case was in ancient Rome in 55 A.D. Nero secured the throne for himself when he poisoned Britannicus. In eighteenth century France, the use of arsenic was commercialized to infamous proportions. The popularity of arsenic (referred to as inheritance powder) declined only when a reliable and sensitive test for arsenic was developed by Marsh in 1836.

Arsenic containing compounds are available in numerous products; therefore, it is not surprising that arsenic poisonings still occur. Many of these poisonings occur accidentally or occupationally (Reich *et al.* 1968; Saady *et al.* 1989; Polkis 1990; Kersjes *et al.* 1987; Kaae 1987; Graham *et al.* 1983; Lugo *et al.* 1969; Hanninen 1985; Fesmire *et al.* 1988; Guhamazumder *et al.* 1988). Still others are the result of individuals who desire to end their lives or have someone who desires to end it for them (Bednarczyk and Matusiak 1982; Mackell *et al.* 1985; Tewari *et al.* 1976.) See Appendix B for case histories (Houts *et al.* 1975).

Table 5. ARSENIC LEVELS FROM VARIOUS SOURCES

ITEM	ppm As
Water	0.01 - 1
Soil	1.0 - 500
Grass	0.1 - 1.6
Ferns	0.2 - 3.64
Vegetables	0.0 - 2.9
Grains	0.11 - 0.16
Ocean Fish	1.0 - 5.0
Fresh Water Fish	2.0 - 9.0
Shellfish	1.6 - 2.9
Shrimp, Lobster	1.5 - 100.0
Meat	0.06 - 1.07
Milk	0.01 - 0.05

The evidence submitted for arsenic testing can be of a variety of materials. Body fluids, tissues, foods, suspicious liquids and solids all may be submitted. The role of sample preparation is very important with arsenic as it is considered a volatile metal. This volatility has been made into an advantage and the technique of hydride generation and analysis of arsene gas has been used for a number of years (Yamamoto and Kumamaru 1976; Robbins and Caruso 1979; Hobbins 1982; Maher 1987; Evans *et al.* 1979; Syty 1965). Currently, there has been a great deal of work in direct analysis of biological fluids (Eaton and McCutcheon 1985; Foa *et al.* 1984; Fernandez and Hiligross 1982; Paschal and Kimberly 1985; Pybus 1988; Vicky *et al.* 1980). This technique is currently used by the TBI laboratory and is outlined in Appendix C. For other samples such as hair, organs, and foods, acid digestion may be used (Solomons and Walls 1983). Appendix C outlines the procedure used by the TBI Crime Laboratory. This technique has the advantage of reducing the volatile As^{+3} ion to the more stable As^{+5} ion.

MOONSHINE

In this country, there has been a long standing tradition of distilling spirits. This has been attributed to the large Scot-Irish immigrations which began in 1720 (Wilkinson 1985). These people settled mainly in the south eastern United States. This area is still the major

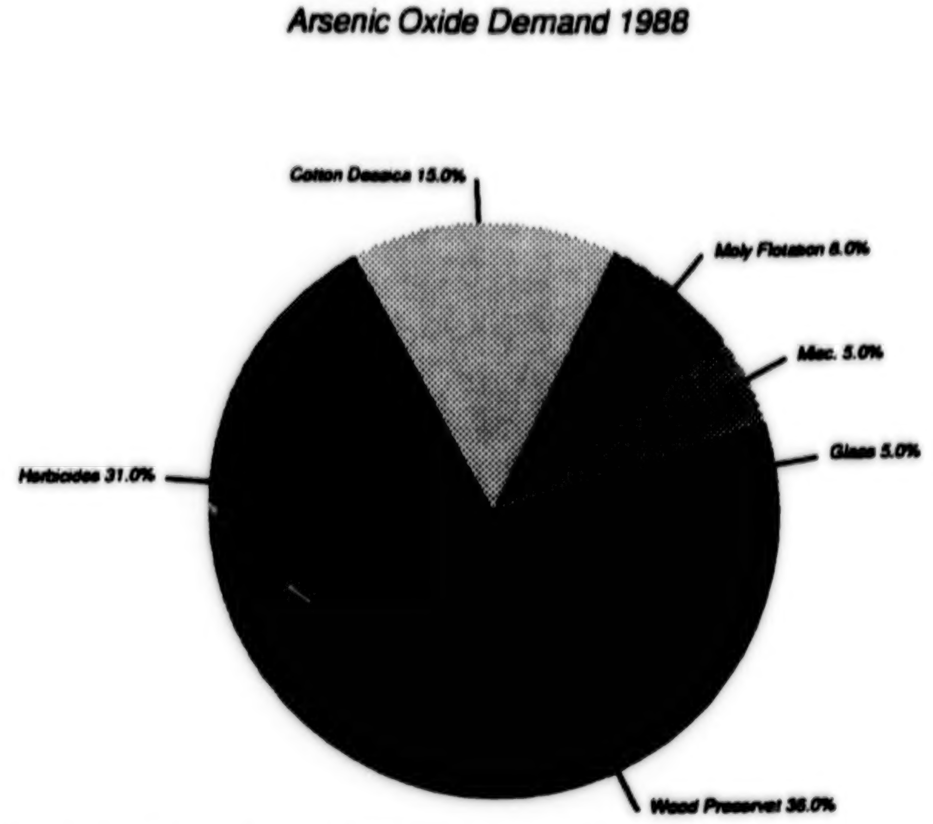

Figure 5. Principal demand for arsenic from manufacturers of various products.

production area of illegal whiskey. Figure 6 shows a typical still.

In 1866, all distilleries were to register for taxation or tear down their stills. This tax was about one dollar per gallon and raised the cost of whiskey considerably (Jack Daniels Distillery, Lynchburg, TN, personal communication). This was not viewed favorably by many Americans and enforcement frequently was met by violent mobs. More than once military forces were called upon to enforce the law (Carr 1972).

By the time the 18th amendment was passed outlawing alcohol sales nationally, many states were already dry. Tennessee enacted prohibition in 1910. This was the heyday of illegal alcohol production and importation. Before the passage of the 21st amendment in 1932 which repealed the 18th amendment of 1920, moonshine still seizures were at an all time high. In 1925, 29,087 stills were seized and over 76,000 people were arrested for tax revenue violations. These seizures were not without cost. Between 1920 and 1934, 126 tax agents were killed, 96 seriously wounded and countless others assaulted. There are no figures for the number of local officials or moonshiners killed. By the time America entered the 1950's, still seizures were once again hovering at around 20,000 annually with one person arrested for every two stills. By this time seizures were mainly confined to North Carolina, Alabama, Georgia, Tennessee and South Carolina (information provided by the IRS covering years 1953-1975; and TN Alcohol Beverage Commission for 1991).

As the 1960's started, one out of five gallons of liquor consumed by the drinking public was moonshine whiskey. In the south, this figure was closer to one in two. However, the market for moonshine bottomed out in the mid 1970's, probably due to an increase in public awareness of poisonings, an increase in seizures of stills, and a marked increase in the price of sugar.

Moonshine consumption is not nor has it been confined to the south. Many moonshiners' production runs are intended for markets in distant cities such as Detroit, Chicago, and New York. Therefore, the problem of poisoning from moonshine is still at national problem.

The main danger in consuming moonshine is chemical poisoning. Moonshine may be contaminated with any number of things such as, paint thinner, ether, methanol, isopropanol, or antifreeze. Additionally, it was reported in the 1960's that 30% to 40% of all moonshine analyzed had some amount of lead in it. We discovered that copper is also a metal found in high concentration in moonshine. Copper has no listed lethal fatal ingestion levels although it is an irritant to the mucus membranes and lining of the stomach (Merck Index 1976). For non-

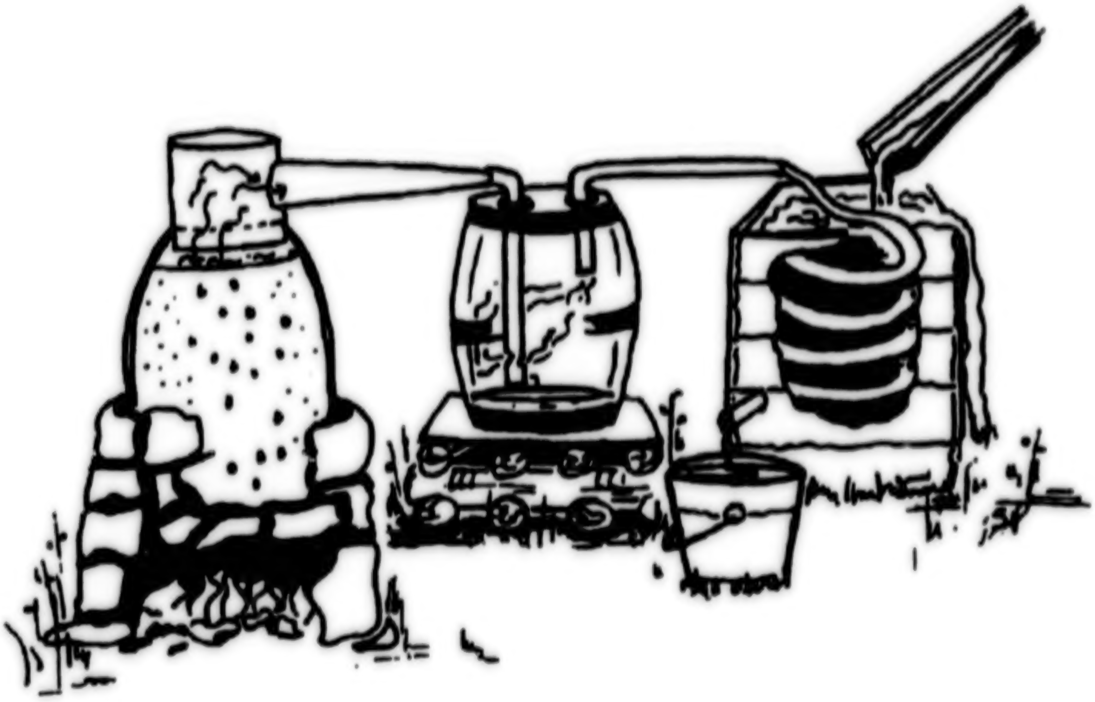

Figure 6. Typical moonshine still.

occupational/environmental lead poisoning in adults, moonshine is considered the source (Hall and Ball 1982). Since copper is not considered a poison it is often overlooked as a metal of interest. The levels of these metals may be used when it is necessary to discriminate between legal and illegal spirits. At least one worker has reported using AAS in combination with other techniques to obtain a fingerprint of a particular distilled spirit and used it to follow distribution and determine a source (Simpkins, personal communication). AAS is typically used alone for the level of these metals in the absence of any other contaminants. See Appendix D.

THE FUTURE

The future of AAS seems bright. As long as forensic scientists require routine ultra-trace metal analysis AAS will be with us. Improvements seem to be constantly reported in the literature (Slavin 1982). Sample preparation, microprocessors, background correction, and atomizer design all have been through generations of change with many more to come (Beach 1987; Sneddon 1987; Carnick *et al.* 1991; Slavin *et al.* 1990; Slavin 1986; Skidmore and Greetham 1983; Morrison 1979; Zehr and Fedorchak 1991; Hoenig and van Hoeywegen 1987; Pau *et al.* 1990).

The only technique which comes close for routine bulk analysis is ICP-ES. Progress in sample introduction is being reported and detection limits may yet enter the realm of furnace AAS (Freiden 1990). Already, where sample volume and sensitivity are not critical ICP-ES is already being used routinely (Koons *et al.* 1988a).

Only time will tell.

REFERENCES

Bartlett, W. A. and Gallatin, D. B. (1956). Cartridge Manual: An Illustrated Digest, Pioneer Press, Union City, TN.

Beach, L. M. (1987). Guidelines for palladium chemical modification in graphite furnace atomic absorption spectrometry, Spectroscopy 2:21-23.

Bednarczyk, L. R. and Matusiak, W. (1982). Case report: An arsenic murder, J. Anal. Toxicol. 6:260-261.

Benitez. (1922). Aqunas Consideramones Sobre las Manchas Produci daz pur los Dispores de Arms de Fuego, Rev. de Med. leg de Cuba 1:30. Abstract in Ann. de Med. leg 3:303 1923

Blacklock, E.C. and Sadler, P. A. (1978). Shotgun pellet identification and discrimination, Foren. Sci. Int. 12:109-117.

Blackmore, H. L. (1965). Guns and Rifles of the World, Viking Press, NY.

Brunelle, R. L., Hoffman, C. M. and Snow, K. B. (1970). Comparison of elemental composition of pistol bullets by atomic absorption: Preliminary study, J. Assoc. Off. Anal. Chem. 53:470-474.

Buchanan, J. D. and Ruch, R. R. (1964). Neutron activation analysis in scientific crime detection, J. Foren. Sci. 1:119.

Bydal, B. A. (1990). Percussion primer mixes, J. Am. Firearm Toolmark Examiner 221.

Carnick, G., Schlemmer, G. and Slavin, W. (1991). Matrix modifiers: Their role and history, Am. Lab. 23:120-131.

Carr, J. (1972). The Second Oldest Profession, Ashley, NY.

Coleman, R. F. (1967). Nuclear techniques in forensic science, J. British Nuclear Energy Society.

Coleman, R. F. and Weston, N. T. (1968). A case concerning neutron activation analysis of glass, J. Foren. Sci. Soc. 8:29.

Cone, R. D. (1973). Detection of barium, antimony, and lead in gunshot residue by flameless atomic absorption spectrophotometry, Police Weapons Center Bulletin 6:4-6.

Covick, L. A. (1982). The analysis of paper samples for aluminum, iron, zinc, and antimony by atomic absorption spectrophotometry, Varian Instruments at Work No. AA-23:1-8.

Cowan, M. E. and Purdon, P. L. (1967). A study of the paraffin test, J. Foren. Sci. 12:19-35.

Crow, R. F. and Connolly, J. D. (1973). Atomic absorption analysis of portland cement and raw mix using lithium metaborate fusion, J. Testing Evaluation 1:382-393.

Dahl, D., Lott, P., Clayton, J., Banney, R., McCarty, D., McMillian, M. and Richardson, P. (1967). Gunshot residue an overview, J. Am. Firearms Toolmark Examiner 12:19-35.

DeGaetano, D. D. (1986). A survey of gunshot residue analysis in forensic laboratories across the United States, Southern Association of Forensic Scientists Newsletter 17:2.

Dobbs, M. D. G., German, B., Pearson, E. F. and Scaplehorn, A. W. (1973). The use of spark source mass spectrometry for the analysis of glass fragments encountered in forensic applications, J. Foren. Sci. Soc. 13:281.

Dutton, W. S. (1942). DuPont One Hundred and Forty Years, C. Scribner's Sons, NY.

Eaton, D. K. and McCutcheon, J. R. (1985). Matrix modification for furnace atomic absorption spectrometric determination of arsenic in whole human blood, J. Anal. Toxicol. 9:213-216.

Evans, W. H., Jackson, F.J. and Dellar, D. (1979). Evaluation of a method for determining total antimony, arsenic, and tin in foodstuffs using atomization in a silica tube using the hydride generation method, Analysist 104:16-34.

FBI. (1935). The dermal nitrate test, Law Enforcement Bulletin 4:10.

FBI. (1940). Further observations on the diphenylamine test for gunpowder residues, Law Enforcement Bulletin 9:6.

Fernandez, F. J. and Hiligross, (1982). An improved graphite furnace method for the determination of lead in blood using matrix modification and the l'vov platform, Atomic Spectroscopy 3:130-131.

Fesmire, F. M., Schauben, J. L. and Roberge, R. J. (1988). Survival following massive arsenic ingestion, Am. J. Emerg. Med. 6:602-606.

Foa, V., Colombi, A., Maroni, M., Buratti, M. and Calzaferri, G. (1984). The speciation of chemical forms of arsenic in the biological monitoring of exposure to inorganic arsenic, Sci. Total Environ. 34:241-259.

Freiden, K. J. (1990). Using ultrasonic nebulization with ICP-ES for analysis of samples with low analyte concentrations, Am. Lab. 22:22-28.

Goleb, J. A. and Midkiff, C. R. (1974). Firearms residue sample collection techniques, J. Foren. Sci., 20:701-707.

Goleb, J. A. and Midkiff, C. R. (1975). The determination of barium by flameless atomic absorption spectrophotometry using a tantalum strip atomizer, Applied Spectroscopy 29:44-48.

Gorby, M. S. (1988). Arsenic poisoning, West J. Med. 149:308-315.

Graham, M. A., Polkis, A., Mackell, M. A. and Ganter, G. E. (1983). A case of suicide involving the concomitant of intravenous injection of barbital and oral ingestion of arsenic, J. Foren. Sci. 28:251-254.

Green, A., and Savve, J. (1972). The analysis of gunshot residue by atomic absorption spectrophotometry, Atomic Absorption Newsletter 11:93-95.

Guhamazumder, D. N., Chakroborty, A. K., Ghose, A., Gupta, J. D., *Chakraborty, D. P., Dey, S. B. and Chattopadhyay, N. (1988).* Chronic arsenic toxicity from drinking tubewell water in rural West Bengal, Bull. World Health Organ. 66:449-506.

Hall, J. T. and Ball, C. V. (1982). Saturine gout: A review of 42 patients, Semin. Arthritis Rhem. 11:307-314.

Hammond, P. B. and Beliles, R. P. (1982). Metals. In: Casarett and Doull's Toxicologgy of Poisons, (Douil, J., Klaassen, C. D. and Amdur, M. O., eds.).

Hanninen, H. (1985). Twenty five years of behavioral toxicology with occupational medicine: A personal account, Am. J. Ind. Med. 7:19-30.

Hausknect, K. A., Ryan, E. A. and Leonard, L. P. (1982). Determination of lead in paint chips using a modified ashing procedure and atomic absorption spectrophotometry, Atomic Spectroscopy 3:53-55.

Hickman, D. A. (1981). The selection of the best elemental variables for the classification of glass samples, Metropolitan Police Forensic Science Laboratory Report No. 4, London, England.

Hickman, D. A. (1982). Elemental analysis and the discrimination of sheet glass samples, Metropolitan Police Forensic Science Laboratory Report No. 22, London, England.

Hobbins, W. B. (1982). Arsenic determination by hydride generation, Varian Instruments at Work AA-22.

Hoenig, M. and van Hoeywegen, P. (1987). Automated trace metal analysis of slurried samples by graphite furnace atomic absorption spectrometry, Varian Instruments at Work AA-77:1-5.

Hoffman, C. M., Brunelle, R. L. and Snow, K. B. (1969). Forensic comparisons of soils by neutron activation and atomic absorption analysis, J. Crimin. Law Criminol. Police Sci. 60:395-401.

Hoggs, I. V. (1978). The Complete Illustrated Encyclopedia of the World's Firearms, A and W Publishers Inc., NY, pp. 6-28.

Houts, M., Baselt, R. C. and Cravey, R. H. (1975). Courtroom Toxicology Environmental and Industrial Toxins pp. ARSE-1 - ARSE-23.

Hunt, O. E., ed. (1987). The Photographic History of the Civil War, Vol. 3., Blue and Grey Press, Secacus, NY

Kaae, E. (1987). Deaths from poisoning in Jutland, Arch. Pharm. Chem. Sci. Ed. 152:50-64.

Kersjes, M. P., Maurer, J. R., Trestrail, J. H. and McCoy, D. J. (1987). An analysis of arsenic exposures referred to the blodgett regional poison center, Vet. Hum. Toxicol. 29:75-78.

Kilroy, W. P. and Moynihan, C. T. (1976). Atomic analysis of borosilicate glass, Anal. Chem. Acta 83:389-392.

Kilty, J. W. (1975). Activity after shooting and it's effect on the retention of primer residue, J. Foren. Sci. 20:219-230.

Kilty, J. (1986). A review of the FBI Laboratory's gunshot primer residue program, Crime Lab. Digest 13:54-61.

Klatt, P. (1972). American Self Primed Ammunition, Part 1-3, Am. Rifleman 120 (3,4,5), pp. 38-40; pp. 42-45, pp. 48-50.

Knight, D. M. and Pyzyz, M. K. (1969). Determination of copper, chromium, cobalt, manganese, molybdenum, nickel, silicon, tungsten and vanadium in tool steel by atomic absorption spectrophotometry, Atomic Absorption Newsletter 8:129-130.

Koons, R. D., Havekost, D. G. and Peters, C. A. (1987). Analysis of gunshot primer residue collection swabs using flameless atomic absorption spectrophotometry: A re-examination of extraction and instrument procedures, J. Foren. Sci. 32:846-865.

Koons, R. D., Havekost, D. G. and Peters, C. A. (1988a). Determination of barium in gunshot residue collection swabs using inductively coupled plasma-atomic emission spectrometry, J. Foren. Sci. 33:35-41.

Koons, R. D., Fiedler, C. and Rawalt, R. C. (1988b). Classification and discrimination of sheet and container glasses by inductively coupled plasma-atomic emission spectrophotometry and pattern recognition, J. Foren. Sci. 33:49-67.

Koons, R. D., Havekost, D. G. and Peters, C. A. (1989). Analysis of gunshot residue collection swabs using flameless atomic absorption spectrophotometry and inductively coupled plasma-atomic emission spectrometry: Effects of a modified extraction procedure and storage of standards, J. Foren. Sci. 34:218-221.

Krishnan, S. S. (1972). Detection of gunshot residues on the hands by trace element analysis, J. Foren. Sci. 22:304-324.

Krishnan, S. S. (1982). Detection of gunshot residue: present status, In: Forensic Science Handbook, (Safferstein, R., ed.), Vol. 1, Prentice Hall Englewood Cliffs, NJ., pp. 573-590

Longridge, J. A. (1890). Smokeless Powder and its Influence on Gun Construction, EFN Spon, London, England.

Lugo, G., Cassady, G. and Palmisano, P. (1969). Acute maternal arsenic intoxication with neonatal death, Am. J. Dis. Child 117:328-330.

Mackell, M. A., Ganter, G. E., Polkis, A. and Graham, M. (1985). An unsuspected arsenic poisoning murder disclosed by forensic autopsy, Am. J. Foren. Med. Pathol. 6:358-361.

Maher, W. A. (1987). Determination of arsenic by graphite furnace atomic absorption spectrometry after zinc column or sodium tetrahydroborate (111) arsine generation and trapping in potassium iodide-iodine solution, Atomic Spectroscopy 8:88-89.

McKenzie, T. (1980). Atomic spectrophotometry for the analysis of wear metals in oil samples, Varian Instruments at Work No. AA-10:1-9.

Merck Index (1976). An Encyclopedia of Chemicals and Drugs, 9th ed. (Windholz, M., Budavari, S., Strounitsos, L. Y. and Fertig, M. N., eds.), Merck and Co., Rahway, NJ.

Meyer, R. (1987). Explosives, VHS Weinheinn, Germany, pp. 308-309.

Morrison, G. H. (1979). Crit. Rev. Anal. Chem. 8:287.

Newbury, M. L. (1980). The analysis of gunshot residue for antimony, and barium by flameless atomic absorption spectrophotometry, Canad. Foren. Sci. J. 13:2.

Newton, J. T. (1981). Rapid determination of antimony, barium, and lead in gunshot residue via automated atomic absorption spectrophotometry, J. Foren. Sci. 26:302-312.

Paschal, D. C. and Kimberly, M. M. (1985). Determination of organic lead by electrothermal atomic absorption with the stabilized temperature platform furnace and matrix modification, Atomic Spectroscopy 65:134-136.

Pau, J. C., Wu, S. C. and Willis, W. (1990). A miniature wet ashing system for trace element analysis, Spectroscopy 5:51-52.

Pillay, K. K. S., Jester, W. A. and Fox, H. A. (1974). New method for the collection and analysis of gunshot residues as forensic evidence, J. Foren. Sci. 19:701-707.

Pitts, S. J. and Kratochvil, B. (1991). Statistical discrimination of flat glass fragments by instrumental neutron activation methods for forensic applications, J. Foren. Sci. 36:122-137.

Polkis, A. (1990). Arsenic poisoning: Acute or chronic? Suicide or murder? Am. J. Foren. Med. Path. 11:226-232.

Price, J. P. (1972). Utilization of atomic absorption spectrophotometry in the synthetic fiber industry, Atomic Absorption Newsletter 11:1-4.

Pybus, J. (1988). Blood lead determination using reduced palladium matrix modifier in graphite furnace atomic absorption, Varian Instruments at Work AA-85, pp. 1-7.

Reich, G. A., Davis, J. H. and Davies, J. (1968). Pesticide poisoning in South Florida, Arch. Environ. Health 17:768-775.

Renshaw, G. D. (1973). The determination of barium by flameless atomic absorption spectrophotometry using a modified graphite tube atomizer, Atomic Absorption Newsletter 12:158-160.

Renshaw, G. D., Pounds, C. A. and Pearson, E. F. (1973). The quantitative estimation of lead, antimony, and barium in gunshot residues by non-flame atomic absorption spectrophotometry, Atomic Absorption Newsletter 12:55-56.

Robbins, W. B. and Caruso, J. A. (1979). Development of hydride generation methods for atomic spectroscopic analysis, Anal. Chem. 51:889a.

Rubeska, I. and Moldan, B. (1967). Atomic Absorption Spectrophotometry, Illiffee Books, London., pp. 9-12.

Rudzitis, E. (1980). Analysis of the results of gunshot residue detection in case work, J. Foren. Sci. 25:839-846.

Ryland, S. G. (1986). Sheet or container? - Forensic glass comparisons with an emphasis on source classification, J. Foren. Sci. 31:1314-1329.

Ryland, S. G. and Koons, R. D. (1991). On the classification of small colorless glass fragments as to their sheet or container origin, J. Foren. Sci. 36:308-311.

Saady, J. J., Blanke, R. V. and Poklis, A. (1989). Estimation of the body burden of arsenic in a child fatally poisoned by arsenite weed killer, J. Anal. Toxicol. 13:310-312.

Schroeder, H. A. and Balassa, J. B. (1986). Abnormal trace elements in man, J. Chronic Dis. 19:85-106.

Skidmore, P. R. and Greetham, S. S. (1983). Analysist 108:171.

Slavin, W. (1982). Atomic absorption spectroscopy: The present and the future, Anal. Chem. 54:685a.

Slavin, W. (1986). Flames, furnaces, plasmas, how do we choose? Anal. Chem. 58:589a-597a.

Slavin, W., Hiefte, G. M. and Raines, T. C. (1990). Insights and predictions: An expert assessment of progress in modern spectroscopy, Spectroscopy 59:22-34.

Smale, D. (1973). The examination of paint flakes, glass, and soils for forensic purposes with special reference to electron probe microanalysis, J. Foren. Sci. Soc. 13:15.

Sneddon, J. (1987). Background correction techniques in atomic spectroscopy, Spectroscopy 25:38-45.

Solomons, E. T. and Walls, H. C. (1983). Analysis of arsenic in forensic cases utilizing a rapid, nonashing technique and furnace atomic absorption, J. Anal. Toxicol. 7:220-222.

Syty, A. (1965). CRC Critical Reviews in Analytical Chemistry 4.

Tewari, S. N., Harpalani, S. P. and Sharma, R. C. (1976). Forensic study of the arsenic contents in burnt bones and ashes in cases and death due to natural causes and of suspected arsenic poisoning, J. Indian Acad. 15:12-16.

Vicky, T. M., Harrison, G. V. and Ramelow, G. J. (1980). Zirconium surface treatment of graphite furnace tubes for the analysis of organolead compounds by atomic absorption spectrometry, Atomic Spectroscopy 1:116-118.

Villanueva, E., Herandez-Cueto, C., Lorente, J. A., Garcia-Quiles, J. and Rodrigo, M. D. (1987). Study of inorganic residues around entrance and exit projectile orifices, J. Foren. Sci. 32:1079-1088.

Wallace, J. S. (1987). Firearms discharge residue detection using flameless atomic absorption spectrometry, J. Am. Firearms and Toolmark Examiners 19:253-261.

Waltz, B. (1985). Atomic Absorption Spectrometry, VCH Pub., Weinheim, Germany

Wilkinson, A. (1985). Moonshine: A Life in Pursuit of White Liquor, Random House.

Yamamoto, Y. and Kumamaru, T. (1976). Comparative study of Zn tablet and $NABH_4$ tablet reduction systems in the determination of As, Sb, and Se by atomic absorption spectrophotometry via their hydrides, Fresenius Z. Anal. Chem. 231:353.

Zehr, B. D. and Fedorchak, M. A. (1991). Microwave acid digestion of inorganics using a bomb vessel, Am. Lab. 23:40-45.

APPENDIX A

Gunshot Residue Analysis

Sample and standard preparation follows the procedure outlined by Koons et al. 1987. Briefly, the swabs are removed from the plastic shaft and placed into clean plastic containers. Standards are prepared by pipeting known amounts of Antimony, Barium, and Lead onto unused swabs. All Swabs are dried overnight at 80ºC. Then 2 ml of 10% Nitric acid are pipetted into each container, vortexed for one minute and returned to 80ºC over for at least two hours.

STD	Sb	Ba	Pb	Quantity in µg
0	0	0	0	
1	0.025	0.25	0.25	
2	0.050	0.50	0.50	
3	0.075	0.750	0.750	
4	0.10	1.00	1.00	

Analysis for Sb should proceed first. Sb solutions have shown a lack of stability for unknown reasons.

Dilution factors from the tube containing the digested swab are as follows:

500 µl to 500 µl distilled water Sb

25 µl to 1000 µl distilled water Ba and Pb

Analysis then proceeds using the below listed furnace parameters. The article by Koons *et al.* 1987 is strongly recommended.

ANTIMONY

STEP	TEMP	RAMP	HOLD	GAS	
1	140	40s	10s	on	
2	1000	30s	5s	on	
3	2200	0s	5s	off	RECORD
4	2600	1s	5s	on	
5	20	1s	20s	on	

BARIUM

1	120	40s	20s	on	
2	1200	15s	15s	on	
3	2680	0s	5s	off	RECORD
4	2700	1s	5s	on	
5	20	1s	20s	on	

LEAD

1	140	10s	40s	on	
2	800	30s	10s	on	
3	1600	0s	5s	off	RECORD
4	2700	1s	5s	off	

APPENDIX B

Workmen were assigned to repair a pump situated in a cellar. During the repair, fumes drove the men from the cellar. Investigation revealed a high level of sodium meta-arsenite and several percent hydrochloric acid. Apparently in priming the pump the hydrochloric acid reacted with the arsenic compound to generate arsine gas.

One worker left less than 30 minutes following exposure. He complained of tingling of the extremities and severe nausea. An hour later he complained of chest pains and collapsed waiting for an ambulance. Revival efforts failed, and he was pronounced dead on arrival. Death was attributed to acute arsenic poisoning with the following results from autopsy: Blood 0.43 mg/L; Lung 0.26 mg/L; Kidney 0.34 mg/L; Urine 0.25 mg/L.

Another worker had been exposed at the same time but only experienced lightheadedness. He had assisted in efforts to revive the first worker. Later, he drove to the hospital to check on the other worker and noted tingling in his hands and feet. His skin became copper-hued with splotches of grey-green. Aggressive supportive treatment and treatment with arsenic antidotes was undertaken and the patient was discharged in good health five days later.

After a domestic quarrel, a sixteen year old girl drank an unknown amount of a solution containing 53% arsenic trioxide. The solution was intended for treating gastric disorders in fowls. Blood was obtained upon admission contained 0.6 mg/L arsenic. Twelve hours later, the following results were reported following an autopsy: Blood 1.3 mg/L; liver 2.3 mg/L; kidney 1.7 mg/L.

A middle-aged male was admitted to a rural hospital in severe gastric distress and with chest pain. He was treated symptomatically and discharged two days later. During his hospitalization, he requested an investigation as he and his employer had bad feelings between them. Investigation revealed on the day of his illness his employer had brought a partial can of coffee to work and prepared coffee. The employer had told everyone in the office the coffee was for Mr. -- and no one else was allowed to consume any. This was contrary to office customs.

Inspection of the can revealed numerous blue/green crystals. Analysis of these crystals revealed the presence of copper and arsenic.

Criminal prosecution was not pursued in spite of a criminal indictment and civil litigation awarded partial compensation for medical expenses.

State of Tennessee v Brooks; Carpenter v Brooks Carter co., TN, 1985

APPENDIX C

BIOLOGICAL SAMPLES

Tissues

Approximately 0.3 gm of solid is analytically weighed and transferred to a clean 50 ml beaker. Approximately 30 ml of concentrated nitric acid (high purity) is added. The beaker is then transferred to a hotplate in a fume hood. The beaker is gradually heated until thick fumes evolve. The solution is left heating until only a moist residue remains. The process is repeated until only a clear solution is left. Then evaporate the solution down until the bottom of the beaker is moist. Add 1 ml of 5% nitric acid solution and analyze on AAS. The furnace parameters are listed below.

Prepare aqueous standards according to the linear range of the particular AAS. Appropriate Matrix Modifiers should be used also.

1000 ppm Pd solution
5% Hydroxylamine Hydrochloride

Equal Volumes of these two are mixed. For each 20 l of solution analyzed 10 μl of matrix modifier is added prior to starting the furnace program.

Hair

Approximately 30-50 pulled hairs are required.
Using mild detergent, wash all hair ultrasonically.
Rinse ultrasonically with distilled water, repeat 3x.
Orient all hairs root to tip.
Cut into 1 cm lengths and document.
(1 cm is the average month's growth for humans)
Digest and analyze as above.

DIRECT ANALYSIS

Treatment of graphite with Zirconium greatly improves it's lifetime. Prepare a 5% Zirconium Chloride solution. Add 10 l to previously conditioned platform and repeat condition run of the furnace. Repeat this five times.

Solutions:
25 ppm As solution
1% Triton X-100 Diluent
2% Ni^{+2} soln.
.2% Mg^{+2} soln.

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Pipet 0.100 ml of blood into sample tube. Pipet 1 ml of diluent into the tube, cap, and vortex for one minute. Transfer to sample cup.

STANDARDS

Pipet 0.100 ml of blood/bile/urine into sample tube. Pipet 0.100 ml of diluent and 0.010 ml of 25 ppm As solution into the tube. Cap and vortex 1 minute. As concentration is .240 ppm. Transfer to sample cup.

SAMPLES

Pipet 0.100 ml of blood/bile/urine into sample tube. Pipet 0.100 ml diluent into the tube, cap and vortex for 1 minute. Transfer to sample cup.

ANALYSIS

Mix equal volumes of the Ni and Mg solutions. Inject 10 μl for every 20 μl sample/standard.

Use the furnace conditions listed below.

LEVELS

	Normal	Excessive
Whole Blood	<10 μg/l	up to 50 μg/l
Urine*	<50 μg/l	>100 μg/l
Hair	<1 mg/kg	

*Best indicator of recent or current exposure. A 24 hour pooled sample is preferred. From Goldfranks Toxic Emergencies c.7, Heavy Metals, 1990 pp. 617-624, Appleton and Lange Norwalk, CT

	Normal	Fatal avg.
Brain	.009 mg/kg	1.7 mg/kg
Liver	.033 mg/kg	29.0 mg/kg
Kidney	.011 mg/kg	15.0 mg/kg.

ARSENIC

STEP	TEMP	RAMP	HOLD	GAS	
1	160	10s	20s	on	
2	1300	10s	20s	on	
3	2200	0s	5s	off	RECORD
4	2700	5s	5s	on	
5	20	1s	20s	on	

CONDITIONING PROGRAM

1	120	1s	10s	on
2	500	1s	10s	on
3	1500	1s	10s	on
4	2000	1s	10s	on
5	2500	1s	10s	on
6	20	10s	20s	on

APPENDIX D
MOONSHINE

Lead

Prepare standards according to the linear range or the AAS. The final solution should be 50% EtOH for the standards. Run samples and standards neat, generally the amount of lead present in moonshine is low, BUT do not be surprised if dilutions are in order. Use the furnace program for GSR Pb, Matrix modifier is Pd and hydroxylamine hydrochloride as outlined in APPENDIX C.

COPPER

Prepare aqueous standards according to the linear range of the AAS. Prepare a series of dilutions of the moonshine, starting with 100:1. Be prepared to go higher or lower in dilutions as levels of Cu can be extremely high. Furnace parameters are listed below:

STEP	TEMP	RAMP	HOLD	GAS	
1	140	5s	30s	on	
2	500	10s	10s	on	
3	2700	0s	5s	off	RECORD
4	20	1s	5s	on	

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COMPARISON OF BULLETS USING THE ELEMENTAL COMPOSITION OF THE LEAD COMPONENT

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Elemental analysis and comparison of the lead component of projectiles from shooting victims and crime scenes to the lead component of bullets associated with suspects has been a useful forensic tool for over 25 years (Lukens *et al.* 1970; Brunelle *et al.* 1970; Gillespie and Krishnan 1969; Lukens and Guinn 1971; Pro *et al.* 1965). Lead compositional analysis is especially valuable in situations where a firearm is not recovered, the crime scene bullet is too mutilated for firearms identification, or the firearm cannot be associated with the suspect. Methods which have been suggested for compositional analysis of bullet lead include neutron activation analysis (NAA), atomic absorption spectroscopy, spark source mass spectrometry, and inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Lukens *et al.* 1970; Brunelle *et al.* 1970; Haney and Gallagher 1975a,b; Peters *et al.* 1988). Presently, the methods used in the FBI Laboratory for the compositional analysis of bullet lead are NAA and ICP-AES. These analytical techniques have been accepted in courts throughout the United States.

During the past 25 years, much analytical data has been collected on bullet lead from known sources. Study of this data has produced a number of conclusions which form the basis for deriving opinions concerning comparison of bullet lead compositions. Primary among these is that not all bullets have the same composition, even those which are physically similar. Over the years, results of analyses of many samples in the FBI Laboratory have demonstrated that many different distinguishable compositions of bullets have been produced and those being produced now continue to display compositional variation. Second, by increasing the number of element concentrations determined, the lead can be more specifically characterized and, hence, more distinguishable compositions can potentially be identified. Third, if two bullets are produced from the same homogenous source of lead, then they will have analytically indistinguishable compositions.

The bullet manufacturing process begins by heating a quantity of lead until it melts. While molten, additives are mixed in and major impurities are removed. Smaller quantities of the modified lead are removed and allowed to cool. These smaller quantities are then extruded into a "bullet wire" the diameter of which is dictated by the caliber of the finished product. This wire is chopped to length and, either immediately or at some later date, the pieces are formed into bullets, loaded into cartridges, and packed into boxes (Fairchild 1971; Petty 1980). This box is the commodity which is sold to the consumer and is the unit of interest to the forensic scientist. However, the manufacturing process is the determining factor in the elemental composition of bullets loaded into the cartridges in each box. Previous studies have concentrated upon either the development of analytical methods or the differences among manufacturers and types of bullets (Lukens *et al.* 1970; Haney and Gallagher 1975a, b; Peters *et al.* 1988; Brandone and Piancone 1984; Blacklock and Sadler 1978; Guinn 1982, 1983; Guinn et al 1987; Guy and Pate 1973), but the variability within a production run or among the bullets in a single box of cartridges has not been addressed in a comprehensive study. Such information is needed for proper interpretation of similarities in elemental composition among evidentiary samples.

This report presents the results of an FBI Laboratory study concerning the compositional variability of bullet leads from four major U. S. manufacturers. Replicate samples from all bullets in multiple boxes of cartridges from each of these manufacturers were analyzed. The goal of this study was to define the variability in element composition within individual bullets, among bullets within boxes of cartridges, among boxes packaged on the same date, among boxes packaged on different dates, and among boxes from the different manufacturers.

MATERIALS AND METHODS

Sample Selection

For this study, full boxes of .38 caliber cartridges loaded with 158 grain, round nose bullets of four brands (Cascade Cartridge Industries (CCI), Federal, Remington, and Winchester) were purchased from commercial ammunition suppliers. For each brand, four boxes of cartridges bearing three different lot numbers (indicating different assembly and packaging dates) were obtained. A fifth box of Winchester ammunition was obtained when it was determined that the bullets in one of the original boxes were a different alloy from the bullets in the other three boxes. Conversations with the manufacturer indicated that this alloy was only marketed for a limited time. The box containing different alloy bullets was not included in the analytical comparison. Production information for the bullets used in this study is shown in Table 1.

Sample Preparation

The nose portion of each bullet was used for most of the analyses. The lead nose of each bullet was quartered using a pair of metal cutters. Three of the quarters were randomly selected for analysis. These samples were cleaned by cutting away surface contamination, resulting in an approximately 120 mg piece from the interior of each quarter. Each sample was flattened by placing it between two steel plates and subjecting the "sandwiched samples" to about 20,000 psi pressure in a hydraulic press. The plates were equipped with a compartmented spacer for simultaneous uniform flattening of multiple samples to a thickness of approximately 0.3 mm. The samples were removed from the press and a circular sample weighing about 15 mg was punched from each flattened sample. These small circular samples were accurately weighed using an electronic microbalance and packaged and labeled for analysis by NAA. The remaining portion of each sample was similarly weighed and placed in a prelabeled sample tube for subsequent dissolution and analysis by ICP-AES.

Table 1. INFORMATION CONCERNING MANUFACTURERS OF BULLETS USED IN THIS STUDY.

Manufacturer	Plant Location	Packaging Dates[a]
Cascade Cartridge	Lewiston, Idaho	Box 1 05/13/83
		Box 2 12/27/85
		Box 3 04/06/86
		Box 4 12/27/85
Federal	Anoka, Minnesota	Box 1 12/13/84
		Box 2 09/23/83
		Box 3 08/15/85
		Box 4 12/13/84
Remington	Lonoke, Arkansas	Box 1 04/27/72
		Box 2 04/27/72
		Box 3 11/17/81
		Box 4 04/27/85
Winchester	East Alton, Illinois	Box 1 02/28/75
		Box 2 01/29/76
		Box 3[b] 06/05/81
		Box 4 01/29/76
		Box 5 07/05/75

[a] Boxes bearing the same packaging date are from the same lot number.

[b] Not included in this study, different alloy than other Winchester samples (new alloy used for one year period).

NAA Analytical Procedure

Samples were heat sealed between two sheets of polyethylene and transported to the National Institute for Standards and Technology (NIST) research reactor facility for irradiation. Analytical sets of 25 bullets (75 samples) along with triplicate samples of NIST SRM 2416 and in-house internal standards as needed were exposed to a thermal neutron flux of 2.8 x 10^{13} neutrons/cm^2-sec for 5 minutes. Following irradiation and a cooling period of several hours, samples were radioassayed using a Canberra Ge(Li) detector coupled to a Nuclear Data 6620 multichannel analyzer. Element concentrations were determined by comparing the gamma ray spectral results from each bullet sample with those from the SRM 2416 standards. The appropriate radioassay parameters are given in Table 2.

ICP-AES Analytical Procedure

Details of the dissolution and ICP-AES analysis have been reported previously (Peters *et al.* 1988), so are only briefly summarized here. The 100 mg samples were placed into 15 ml polypropylene tubes to which 10 ml of 20% nitric acid was added. The tubes were capped and placed into an oven at 80°C for three hours. The tubes were then removed from the oven, allowed to cool, and 0.010 ml of 49% HF added. The tubes were recapped and the contents mixed by vortexing. Standards were prepared by accurately weighing 10 g of 99.9999% lead (Alfa Products, Danvers, MA) and 10 g of SRM 2416 bullet lead into separate 1000 ml Erlenmeyer flasks. To each flask was added 400 ml of deionized water and 200 ml of concentrated nitric acid. The flasks were heated on a hotplate at 140°C until the lead dissolved. The solutions were cooled, transferred quantitatively to 1000 ml volumetric flasks and brought to volume with deionized water. The high purity lead solution was used to dilute

Table 2. NEUTRON ACTIVATION ANALYSIS ACTIVATION AND RADIOASSAY PARAMETERS.

Sample Irradiation

Facility	NIST RT-4
Neutron Flux	2.8 x 10^{13} n/cm^2-sec
Time	5 min

Standard Data for SRM 2416

	Composition %	Isotope	n, τ Product Half-life hours	Energy KeV
Copper	0.065	^{64}Cu	12.8	511
Antimony	0.79	^{122}Sb	64.8	564
Arsenic	0.056	^{76}As	26.3	559

Detector Specifics

Type	Coaxial Germanium, 91.3 cm^3
Efficiency	19% for ^{60}Co at 1332 KeV
Resolution	1.77 eV FWHM for ^{60}Co at 1332 KeV
Radioassay Time	15 min each for samples and standards

the SRM 2416 standard to produce standards of intermediate composition for analysis of bullet leads. Aqueous standards made from 1000 μg/ml Sn standard solution (Fisher Scientific) were used for calibration for the bullet lead samples having high tin contents. Element concentrations were determined using a Plasma II ICP-AES (Perkin-Elmer) with the instrument operating conditions given previously (Peters *et al.* 1988). Well-characterized bullet lead standards were included with each set of samples to insure analytical accuracy.

RESULTS AND DISCUSSION

In this study, 7 to 9 analytical determinations were made on each of triplicate samples of lead from 800 bullets resulting in nearly 20,000 element concentration measurements. Because of space limitations, these results are presented in summary form. Elemental concentrations are referred to by analytical method and element symbol, that is, NAACU refers to copper concentration determined using NAA.

Analytical Accuracy

This study provides a comparison of NAA and ICP-AES results for Cu and Sb using a large number of samples analyzed by the two independent analytical methods. For the samples in this study, the equations for linear regression of the ICP-AES results on the NAA results (expressed as μg/g) are as follows:

ICPSB = 1.028*NAASB - 161.3 with r = 0.998, for all 2400 samples

ICPSB = 0.985*NAASB +71.1 with r = 0.995, for those 1200 samples having Sb at less than the one percent level

ICPCU = 1.012*NAACU - 3.231 with r = 0.995, for all 2400 samples

The slope values in these equations are equal to the ideal value of 1 and the y-intercept values are equal to the ideal value of 0 within the measurable analytical uncertainties, thus indicating the generally excellent agreement between the two techniques. The accuracy of NAA for Sb, Cu, and As has been well established and that of ICP-AES has previously been demonstrated for several elements including the six in this study (Peters *et al.* 1988).

Compositional Variation within Bullets

In a limited study, 10 bullet leads from a single box were subdivided into three portions - nose, middle, and base. Each portion was analyzed in triplicate. Based on the nine samples of each bullet, all measured element concentrations were found to be randomly distributed throughout the bullets within the analytical uncertainties. Based on the lack of measurable differences in composition within these bullets and 25 years of similar measurements in the FBI Laboratory, three replicates from the nose portion of each bullet lead were used in the full study.

The triplicate samples of each bullet lead were used to calculate a coefficient of variation (COV) for each element as a measure of the compositional variation within bullets. The mean within-bullet COV values and the ranges in compositions of the four brands are shown in Table 3. The within-bullet COVS for NAASB, ICPSB, NAACU, and ICPCU are in the 1 to 3% range, over the wide composition ranges for these elements in the four brands. The within-bullet COVS for ICPAG are in the 1 to 3% range across all brands, all of which contain Ag in similar concentration ranges. The within-bullet COVS for NAAAS and ICPBI increase as the concentration decreases, being 1 to 3% at higher levels, and about 5% at lower levels. These precision values are similar to those resulting from repeated analysis of homogeneous NIST standard reference leads, indicating that the bullets in this study were compositionally homogeneous within the instrumental analytical uncertainties.

Compositional Variation within Boxes

Examination of the data indicated that in all but one box of cartridges, there were more than one obvious

Table 3. WITHIN BULLET VARIABILITY MEASUREMENTS. VALUES REPRESENT THE MEAN COEFFICIENT OF VARIATION OF TRIPLICATE MEASUREMENTS OF EACH BULLET AND THE RANGE IN CONCENTRATIONS FOR ALL BULLETS OF EACH BRAND.

Brand		NAASB/ICPSB	NAACU/ICPCU	NAAAS/ICPAS	ICPAG	ICPBI	ICPSN
CCI	COV, %	1.6/1.7	2.5/1.7	2.8/---	1.9	3.8	---
	Range, ppm	23800 - 29900	97 - 381	82 - 546	18 - 69	56 - 180	
Fed	COV, %	1.2/1.5	1.9/1.5	1.6/3.7	2.2	6.7	2.5
	Range, ppm	25700 - 29000	233 - 329	1127 - 1645	14 - 19	30 - 91	1100 - 2880
Rem	COV, %	0.8/1.5	1.6/1.5	3.7/---	1.8	3.4	---
	Range, ppm	5670 - 9620	62 - 962	4 - 272	21 - 118	67 - 365	
Win	COV, %	1.0/1.9	2.1/2.1	5.7/---	1.9	4.4	---
	Range, ppm	2360 - 6650	54 - 470	5 - 165	14 - 61	35 - 208	

distinct lead composition. Therefore, mean and standard deviations of elemental concentrations within boxes of bullet lead have little meaning, so they were not calculated. Instead, within each box of cartridges, the lead samples were subdivided into compositional groups constructed as follows. The mean element concentrations of the first and second bullets in a box were compared using the range based on the triplicate analysis or a predetermined analytical uncertainty, whichever was larger, as a criterion. If they overlapped in all elements, they were placed into a compositional group, otherwise they were placed into separate groups. The next bullet was then compared to these two, and so on, in the same manner until all bullets in a box were placed into compositional groups. Each bullet within a group is analytically indistinguishable for all elements measured from at least one other bullet in the group and is distinguishable in one or more elements from all bullets in any other compositional group. It should be noted that occasionally in groups containing more than two bullets, chaining of bullets occurs. That is, two bullets may be slightly separated from each other, but each be indistinguishable from a third bullet, resulting in all three being included in the same compositional group.

The mean element concentrations and number of bullets in each compositional group within each box of cartridges from this study are shown in Tables 4-7. The number of compositional groups per box varies from one brand to another, but is fairly consistent for a given brand. The average number of compositional groups per box is 2.0 for Federal, 3.5 for CCI, 6.0 for Remington, and 12.5 for Winchester. The number of bullets in each compositional group varies widely, even within a single box. The number of compositional groups within each box, their ranges in elemental concentrations, and the number of bullets per compositional group reflect the production and packaging processes in effect at each manufacturing plant at the time of production of the boxes used in this study. The fact that there are distinguishable compositional groups of lead, even within a single box, has significant impact on interpretation of results in forensic cases. This interpretation must be undertaken with an understanding of the underlying production and packaging processes which lead to the observed lead compositional distributions.

The variation in element concentrations within compositional groups is one factor which determines the ability to distinguish between bullet leads from different compositional groups. Of the 74 compositional groups found in this study, 19 contain more than 10 bullets (30 samples). These groups are large enough to provide reliable estimates of the overall compositional group variabilities. As a measure of the elemental variation within compositional groups, we have calculated the group cov for each element for these 19 compositional groups. These results are shown in Figure 1, where the group cov by element is plotted against the mean group element concentrations. Elemental variations within a compositional group, shown in Figure 1 are, on average, slightly greater than the within-bullet COVS, shown in Table 3. If the only contributor to cov were the analytical precision, the within bullet and within compositional group COVS should be equal. The slightly larger variability within compositional groups demonstrates that a portion of the group variability may reflect true heterogeneity among the bullets within a compositional group. Complete explanation of the causes of variation among bullets within a compositional group can only be determined by analysis of samples removed during the manufacturing process. Although not a goal of this study, such information has been gathered over many years from samples removed from cartridge assembly lines and analysis of many boxes of bullet leads in the FBI Laboratory.

Table 4. CCI BULLET LEAD COMPOSITIONAL GROUPS. MEAN ELEMENT CONCENTRATIONS IN μg/g.

GROUP	NOBULLETS	NAASB	NAACU	NAAAS	ICPBI	ICPAG
1-Box1	1	27500	141	369	128	23
2-Box1	17	25300	166	405	109	24
3-Box1	23	26000	204	422	107	24
4-Box1	9	25700	286	497	98	19
5-Box2	5	25400	153	411	88	28
5-Box4	4	25500	157	396	82	28
6-Box2	1	26200	229	325	93	34
6-Box4	1	25500	223	321	83	33
7-Box2	44	27200	340	138	147	38
7-Box4	43	28000	349	139	145	39
8-Box3	9	27300	179	93	170	57
9-Box3	40	26800	209	172	124	52
10-Box3	1	27600	221	132	77	68
11-Box4	2	27000	103	538	65	18

Compositional Variation Among Boxes of the same Brand

The compositional variation of bullets among boxes of cartridges of the same type and brand is one of the most significant factors in determining the forensic implication of compositional association. Compositional group overlaps from one box to another, where they occur, should be recognized and explanations sought. The assembly and packaging dates, locations and respective manufacturers of boxes of cartridges whose bullet leads were analyzed in this study are shown in Table 1. The range of assembly and packaging time is relatively short for three of the manufacturers. CCI has a three year range, Federal a two year range, and Winchester an 11 month range; Remington is the only brand with a large spread among packaging dates, 12 years.

For both the CCI and Remington leads, shown in Tables 4 and 6, there are no compositional group overlaps among bullets from boxes with different assembly and packaging dates. All indistinguishable compositional group pairs occur between boxes with common production dates. In both of these brands, overlapping compositional groups consist of one large group of bullets and several smaller groups or single bullets.

The elemental compositions of the Federal bullet leads, shown in Table 5, follow a different behavior. Box #3 of Federal is the only box of cartridges in this study containing a single compositional group. The remaining three boxes contain two distinct compositional groups common to all three boxes. Boxes #1 and #4 bear the same production and packaging date, but box #2 was packaged 15 months prior to the other two. There are two possible explanations for the overlapping compositions for bullets packaged on different dates. Overlapping compositions occur either by coincidence or because the bullets originated from the same analytically homogeneous source of lead. From our previous experience and discussions with Federal Cartridge Corporation representatives, a reasonable explanation for multiple boxes containing indistinguishable lead compositions is that the cartridges were produced from a

Table 5. FEDERAL BULLET LEAD COMPOSITIONAL GROUPS. MEAN ELEMENT CONCENTRATIONS IN μg/g.

GROUP	NOBULLETS	NAASB	NAACU	NAAAS	ICPBI	ICPAG	ICPSN
1-Box1	18	27400	268	1320	61	16	1760
1-Box2	13	27300	271	1340	61	16	1740
1-Box4	19	27300	270	1340	58	16	1720
2-Box1	32	27300	294	1470	67	17	2490
2-Box2	37	27400	302	1500	66	16	2360
2-Box4	28	27300	297	1490	64	17	2430
3-Box3	50	27600	248	1230	71	16	2470
4-Box4	3	27900	247	1280	62	17	1180

Table 6. REMINGTON BULLET LEAD COMPOSITIONAL GROUPS. MEAN ELEMENT CONCENTRATIONS IN μg/g.

GROUP	NOBULLETS	NAASB	NAACU	NAAAS	ICPBI	ICPAG
1-Box1	6	5800	727	80	197	32
1-Box2	7	5840	730	83	198	33
2-Box1	10	6020	608	112	192	33
2-Box2	9	6040	612	111	190	34
3-Box1	26	6300	508	141	185	35
3-Box2	30	6320	513	142	182	35
4-Box1	4	6450	458	162	182	35
4-Box2	3	6510	464	161	176	36
5-Box1	1	8050	66	220	175	36
6-Box1	3	8060	68	263	168	37
7-Box2	1	7640	200	168	158	39
8-Box3	1	7710	143	105	124	32
9-Box3	1	7820	172	98	116	30
10-Box3	8	8000	147	56	78	109
11-Box3	1	8460	177	128	122	29
12-Box3	6	8600	144	115	80	87
13-Box3	15	8890	197	145	122	28
14-Box3	16	9420	203	165	117	28
15-Box3	2	9170	269	169	124	27
16-Box4	1	7080	951	17	221	32
17-Box4	11	7190	419	13	154	24
18-Box4	13	7420	447	44	330	44
19-Box4	3	8080	269	20	334	44
20-Box4	22	8190	233	6	120	23

common lead production source and component storage before cartridge loading. The small concentration ranges exhibited by Sb, Ag, and Bi in Federal lead in this study are also factors limiting the discrimination capability.

The compositional group distributions across boxes of Winchester bullets exhibit a third pattern of behavior. The Winchester bullets are characterized by the presence of many different compositional groups within each box. Explanations for this may include smaller production runs and more frequent component addition to the melted lead. The comparatively large number of compositional groups per box of Winchester lead offers a means of determining whether cross-box compositional overlaps occur as a result of coincidental production of indistinguishable composition lead on two dates or by a common production source. If one compositional group is found in common between two boxes, it may be attributable to coincidence. However, when multiple groups are found in common, a common production source of lead components is more likely. Winchester boxes #2 and #4, which bear the same assembly and packaging date have respectively 14 and 15 compositional groups. Of these, nine are common to both boxes, an expected occurrence given the same packaging date for these two boxes. As in most Winchester compositional groups, these groups each contain only one or several bullets. However, boxes #4 and #5 also have two compositional groups in common. The compositional groups in box #4 that match those in box #5 are different than the groups that match those in box #2. The packaging dates of boxes #4 and #5 differ by 7 months. The facts that there are two group overlaps and that there are five elements with wide ranges and good analytical precision in Winchester lead, make it unlikely that the overlap is a coincidental occurrence. Discussion with Winchester personnel and past experience indicate that the compositional group overlaps for these two boxes are reasonably explained by a common production source and storage of components before cartridge loading.

Compositional Variation across Brands

The ranges of measured element concentrations for each brand are shown graphically in Figure 2. Several observations are apparent from this data. Nominal Sb content, a compositional factor intentionally controlled by the lead manufacturer, is 0.5, 0.75, 2.75, and 2.75% for Winchester, Remington, Federal, and CCI respectively. The range in Sb concentrations relative to the mean is greater in Winchester than other brands. For example, a range of 0.24 to 0.66% Sb was found in the lead from a single box of Winchester cartridges. The Federal bullet leads in this study are much different from the other brands in that they contain much higher Sn and As concentrations. The ranges in concentration of Cu and Ag are less in Federal than in the other brands. In summary, the four brands of bullets in this study are each compositionally distinguishable from each other. However, it is our experience that each manufacturer uses several alloys of lead across their product line re-

Table 7. WINCHESTER BULLET LEAD COMPOSITIONAL GROUPS.
MEAN ELEMENT CONCENTRATIONS IN μg/g.

GROUP	NOBULLETS	NAASB	NAACU	NAAAS	ICPBI	ICPAG
1-Box1	4	2440	270	11	126	30
2-Box1	1	3610	178	54	99	35
3-Box1	1	4280	98	32	84	46
4-Box1	2	4320	317	37	128	35
5-Box1	24	4330	156	33	100	52
6-Box1	2	4100	171	32	101	54
7-Box1	2	4520	469	7	199	44
8-Box1	1	4520	316	22	156	34
9-Box1	1	4770	176	18	118	21
10-Box1	1	5280	70	22	48	14
11-Box1	2	5410	207	26	53	21
12-Box1	7	5390	187	59	51	22
13-Box1	1	5560	141	24	111	20
14-Box1	1	6570	112	28	84	22
15-Box2	3	3830	205	37	136	53
15-Box4	6	3850	210	37	149	56
16-Box2	8	4080	61	14	132	35
16-Box4	6	4120	61	14	133	36
17-Box2	4	4200	176	158	150	39
17-Box4	4	4260	177	158	156	40
18-Box2	4	4200	162	84	128	36
18-Box4	1	4230	161	84	138	38
19-Box2	6	4220	154	67	117	36
19-Box4	2	4380	163	67	114	36
20-Box2	1	4460	90	16	128	35
20-Box4	2	4480	92	18	135	36
21-Box2	5	4470	130	40	131	47
21-Box4	2	4470	131	40	134	46
22-Box2	4	4530	214	96	114	30
22-Box4	4	4610	214	96	129	31
23-Box2	1	4540	234	72	140	33
24-Box2	9	4770	401	28	141	32
24-Box4	4	4840	408	28	145	33
25-Box2	1	4770	168	13	163	57
26-Box2	1	4810	278	106	121	29
27-Box2	2	4980	404	57	116	28
28-Box2	1	5540	409	8	123	29
29-Box4	1	4460	230	49	122	32
30-Box4	1	4510	186	36	126	43
31-Box4	1	4870	325	75	129	29
32-Box4	13	4950	322	8	98	42
32-Box5	24	5050	327	8	100	43
33-Box4	1	5360	316	35	148	38
34-Box4	2	5590	226	32	103	44
34-Box5	4	5630	226	32	109	44
35-Box5	6	4470	387	14	116	45
36-Box5	8	4570	299	9	97	48
37-Box5	2	5120	220	29	114	43
38-Box5	3	5250	402	22	128	40
39-Box5	3	5460	301	26	121	39

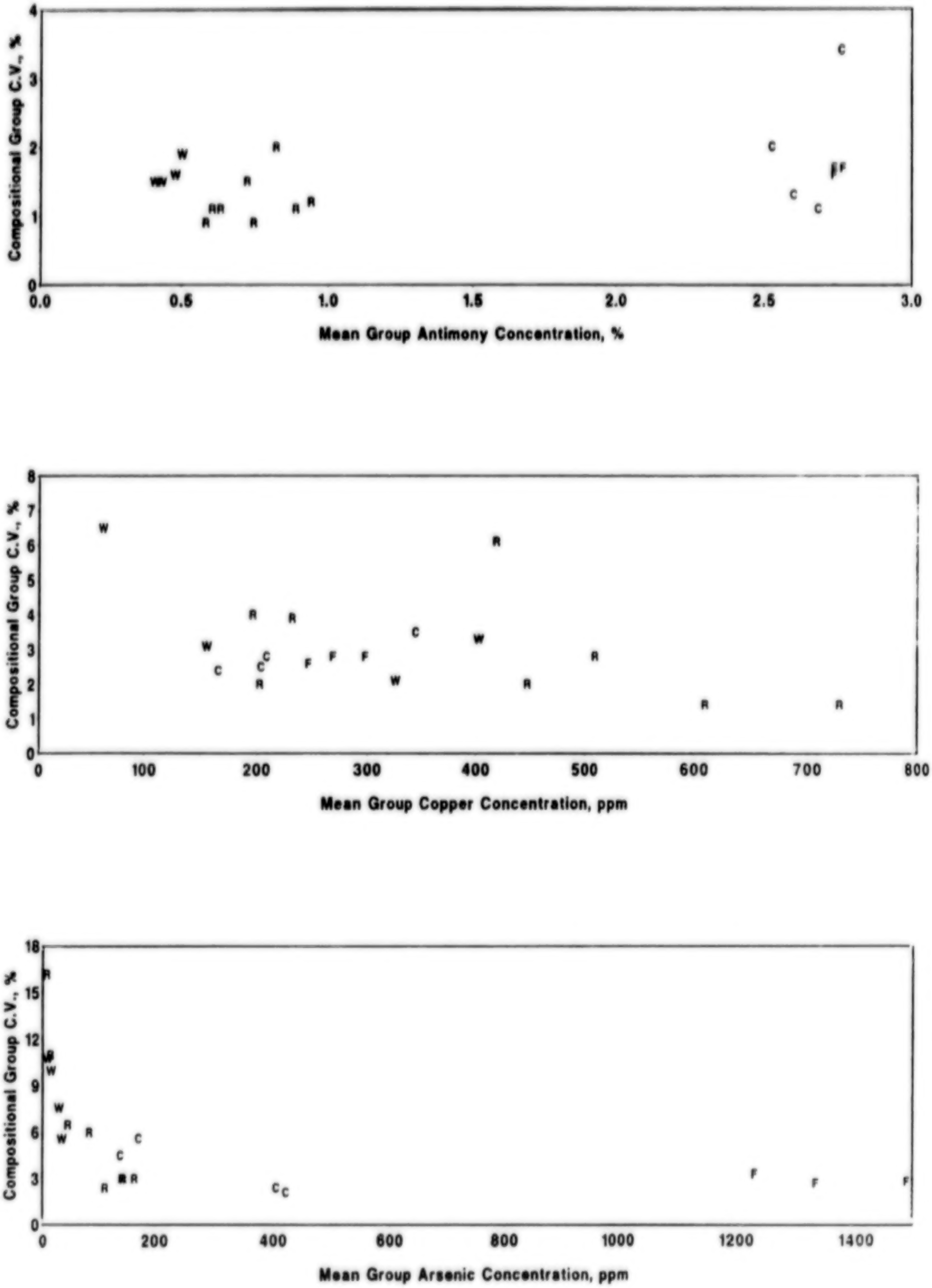

Figure 1. Element concentration statistics for the 19 compositional groups containing more than 10 bullet leads.

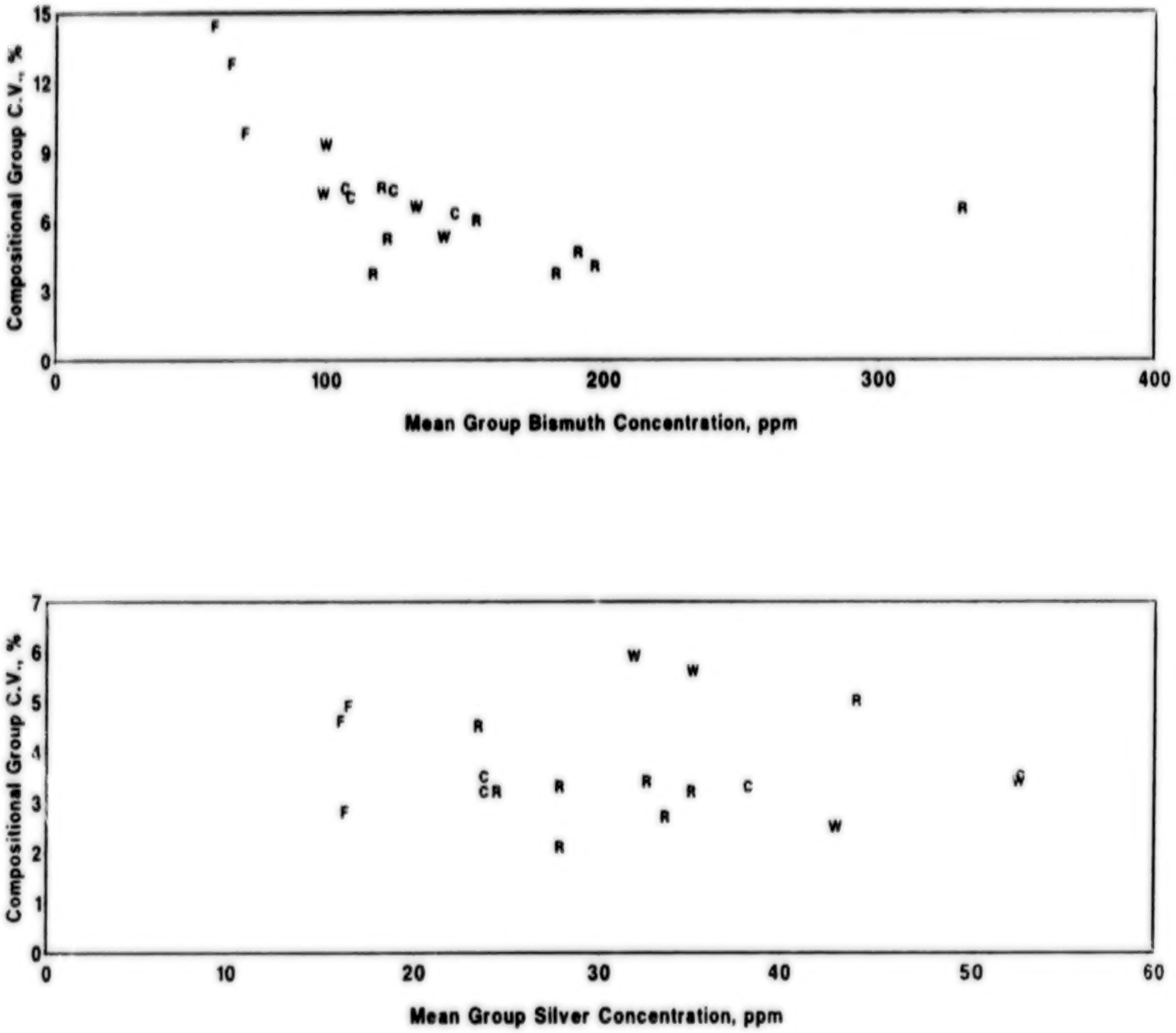

Figure 1 — Continued. Element concentration statistics for the 19 compositional groups containing more than 10 bullet leads.

sulting in wider ranges of elemental compositions than those seen in this study. Therefore, it is generally not possible to identify the manufacturer of a single bullet based on the bullet's elemental composition.

Discriminating Capabilities of Individual Elements in Bullet Lead Comparisons

Two bullets must be analytically indistinguishable in all measured elements before they can be attributed to a common source. However, the relative importance of individual elements for source discrimination depends upon the measured homogeneity of the lead compared to the across-product range. In this study, all elements provide useful data for grouping. The relative importance of the elements for providing discrimination of lead sources decreases in the order: Cu, As > Sb > Bi, Ag. Tin is not included in this sequence because of its limited detectability in three brands of the lead in this study. However, Sn is very important in defining compositional groups in the Federal lead, where it was high enough to be accurately determined. Although Bi and Ag provide the least discrimination, they are useful in support of group divisions based on the other elements in cases where intergroup differences are not large. The more elements which are measured and the greater their ratio of range to analytical precision, the better the discrimination capability and the less the potential for coincidental overlaps.

SUMMARY

Accurate, reproducible elemental concentration determinations in bullet leads can be obtained using both NAA and ICP-AES methods. In this study, the elemental compositions of the lead component of all cartridges from 16 boxes of cartridges from four manufacturers were determined. Element concentrations in individual bullet leads are generally homogeneously distributed

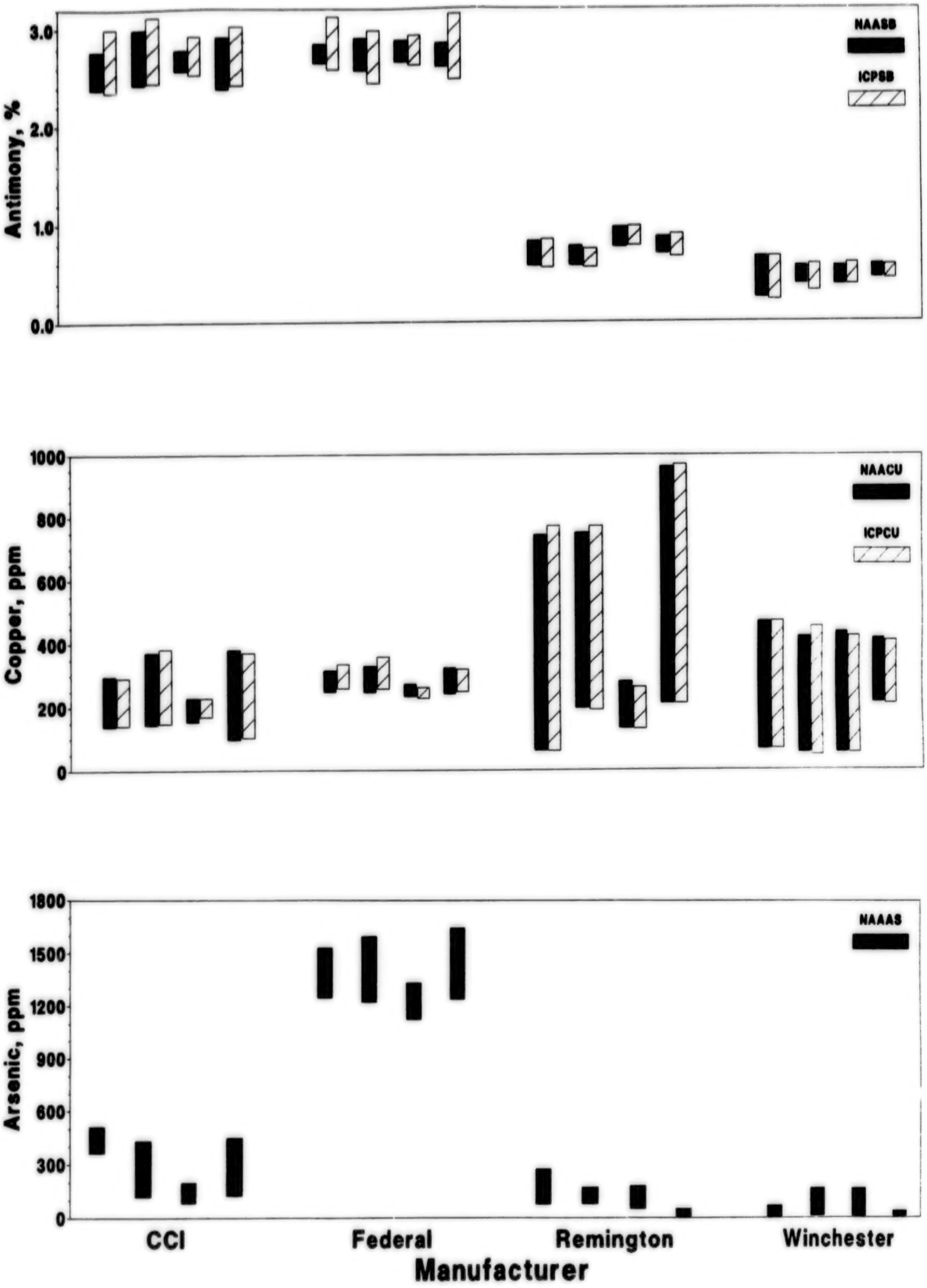

Figure 2. Range in element concentrations in bullet leads from four boxes from each of four brands.

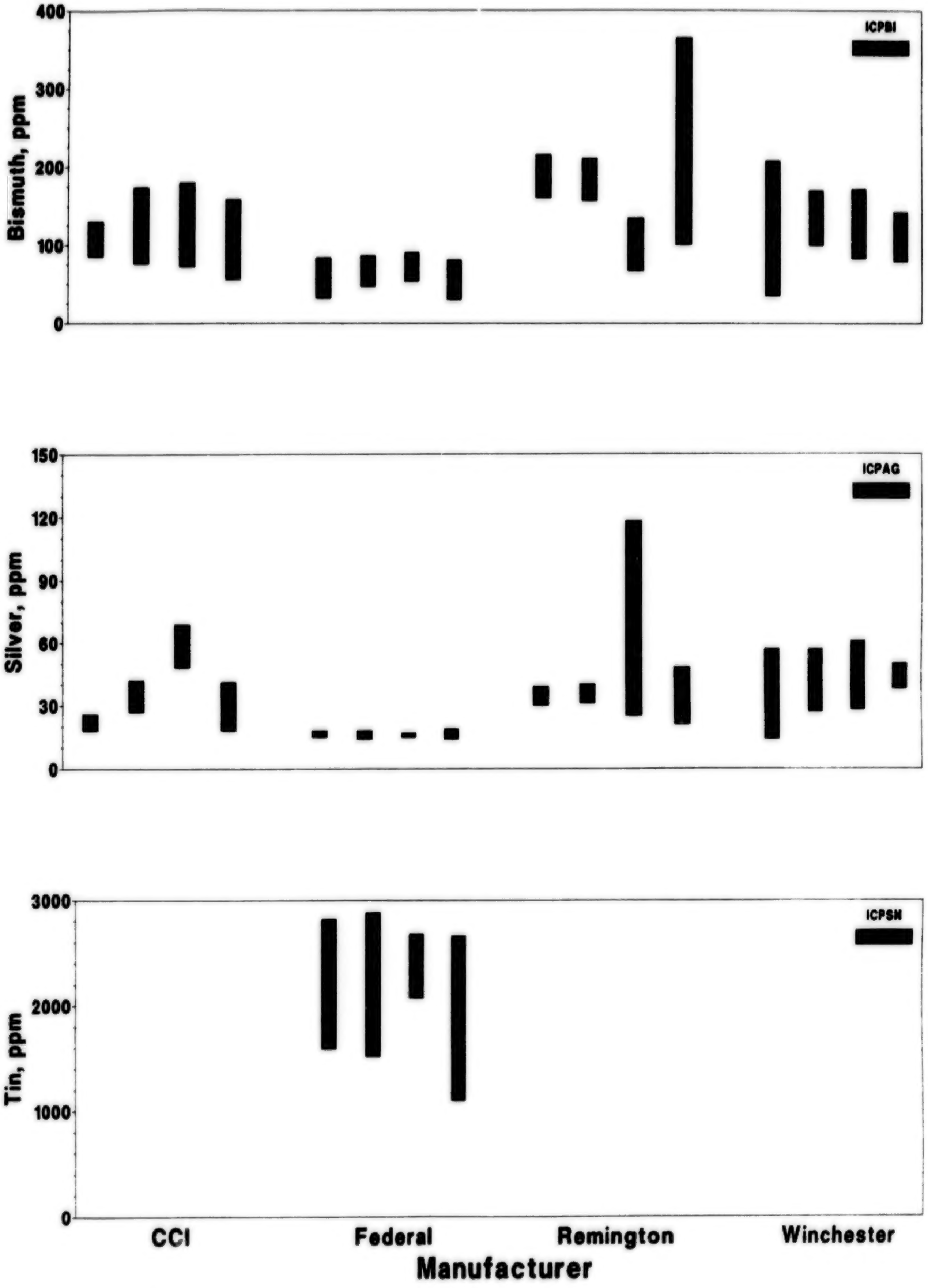

Figure 2 — Continued. Range in element concentrations in bullet leads from four boxes from each of four brands.

within the analytical uncertainty of NAA and ICP-AES. The bullets within a single box of cartridges can be subdivided into a number of distinct compositional groups. These groups are analytically distinguishable from one another in one or more element concentrations. Further, the number of compositional groups per box varies from one brand to another, reflecting differences in the manufacturing processes. No cross-brand compositional group overlaps were found in this study. Compositional group overlap among bullet leads from cartridges of the same brand are generally expected from boxes with the same assembly and packaging dates and not expected from boxes with widely different dates. Results from this project and our previous experience indicate that when compositional overlap between boxes occurs, it is more reasonable to expect the overlap from boxes of the same type and brand of bullet, packaged near the same date. The classifying power of the elements studied is, in general, Cu,As>Sb>Bi,Ag. Tin provides excellent discrimination for the Federal bullets in this study, which have high concentrations of this element.

This study demonstrates the compositional variation of bullets within boxes, from box to box of the same brand, and from brand to brand. As an illustration of forensic application of this approach, let us take an example of one bullet removed from a victim, five cartridges from a revolver, and 44 cartridges from a box associated with the suspect. Each bullet component of all these specimens is analyzed by NAA and ICP-AES. The composition of the bullet from the victim is analytically indistinguishable in all five elements determined from two bullets from the gun and twenty from the box. Two more bullets from the gun are compositionally indistinguishable from 10 others from the box. The last bullet from the gun is compositionally indistinguishable from seven others from the box. The seven remaining bullets from the box fall into two additional compositional groups. It is our opinion that these results are forensically significant in associating the victim, weapon, and suspect in this example.

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REFERENCES

Blacklock, E. C. and Sadler, P. A. (1978). Shot-gun pellet identification and discrimination, Forens. Sci. Intern. 12:109-117.

Brandone, A. and Piancone, G. F. (1984). Characterisation of firearms and bullets by instrumental neutron activation analysis, Intern. J. Appl. Radiat. Isot. 35:359-364.

Brunelle, R. L., Hoffman, C. M. and Snow, K. B. (1970). Comparison of elemental composition of pistol bullets by atomic absorption: preliminary study, J. Assoc. Off. Anal. Chem. 53:470-474.

Fairchild, G. (1971). U. S. ammo makers turn out cartridges by the billions, Am. Rifleman 119:28-30.

Gillespie, K. A. and Krishnan, S. S. (1969). Analysis of lead shot - a comparison of analyses using atomic absorption spectrophotometry and neutron activation analysis, Canad. Soc. Forens. Sci. J. 2:95-103.

Guinn, V. P. (1982). NAA of bullet-lead evidence specimens in criminal cases, J. Radioanal. Chem. 72:645-663.

Guinn, V. P. (1983). The elemental comparison of bullet-lead evidence specimens, In: Chemistry and Crime (Gerber, S. M., ed.), American Chemical Society, Washington, D. C., pp. 64-77.

Guinn, V. P., Fier, S. R., Heye, C. L. and Jourdan, T. H. (1987). New studies in neutron activation analysis, J. Radioanal. Nucl. Chem. 114:265-273.

Guy, R. D. and Pate, B. D. (1973). Studies of the trace element content of bullet lead and jacket material, J. Radioanal. Chem. 15:135-142.

Haney, M. A. and Gallagher, J. F. (1973a). Differentiation of bullets by spark source mass spectrometry, J. Forens. Sci. 20:484-500.

Haney, M. A. and Gallagher, J. F. (1973b). Elemental analysis of bullet lead by spark source mass spectrometry, Anal. Chem. 47:62-65.

Lukens, H. R. and Guinn, V. P. (1971). Comparison of bullet lead specimens by nondestructive neutron activation analysis, J. Forens. Sci. 16:301-308.

Lukens, H. R., Schlesinger, H. L., Guinn, V. P. and Hackleman, R. P. (1970). Forensic neutron activation analysis of bullet-lead specimens, U. S. Atomic Energy Commission Report GA-10141, 48 p.

Peters, C. A., Havekost, D. G. and Koons, R. D. (1988). Multielement analysis of bullet lead by inductively coupled plasma-atomic emission spectrometry, Crime Laboratory Digest 15:33-38.

Petty, C. E. (1986). American ammunition makers, Am. Rifleman 134:28-29,72,74.

Pro, M. J., Schlesinger, H. L. and Hoffman, C. M. (1965). Application of neutron activation analysis in criminalistics, U. S. Treasury Dept. Report, 96 p.

DUCT TAPE ANALYSIS AS TRACE EVIDENCE

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Duct tape, or more properly, polyethylene coated cloth tape is an all American product. It's as American as baseball, apple pie, and the fourth of July. It was invented here and all of it is still made in the U.S.A. Most duct tape is consumed in the U.S.A.

Duct tape, as we know it, is that silvery grey, thick, strong, sticky tape that will stick to virtually everything. It originated in the 1930's from a water proof medical tape developed by the Johnson & Johnson Company. With the on set of World War II, particularly in the Pacific Theatre of operations, the military adapted it to sealing and water proofing ammunition containers. They of course required an olive drab colored tape which is still made today. Following the war, the rapid surge in residential home building made this tape a natural low cost, convenient means of fabricating duct work for central heating systems. The tape was made silver grey in color — to match sheet metal, adopted its present name, and now the rest of the story is history.

Duct tape is available in virtually every retail store in America from K-mart to Food Giant to the corner drug store. Its probably a safe bet that somewhere in most American homes, automobiles and places of work, there is a roll of duct tape hidden somewhere. Duct tape is a tribute to American ingenuity for the endless number of uses that have been devised for it. Duct tape has been used for patching, sealing, and repairing almost any thing that breaks, from car bodies to broken bones. It has been to the bottom of the ocean, the top of Mt. Everest, and to the moon and back. In some cases, it has a personality all its own. It is called Duck Tape and Two Hundred mile an hour tape. I like to call it Fun Tape.

Unfortunately, however, duct tape has fallen into some sinister and macabre uses, and is now today being referred to as Crime Tape. It has been used for binding rape and murder victims, wrapping drug parcels, and holding bombs together. This paper provides a brief overview of what duct tape is made up of, and how it might be useful as evidence in identifying a suspect and linking him to the scene of the crime. This is primarily from a formulator's and manufacturer's point of view, rather than as an analytical chemist, since my expertise in that area is limited.

Let me preface my remarks with two key points as follows:

1 — All duct tapes are not alike even though they may appear to be the same to the casual observer.

2 — Everything changes. New constructions appear and old constructions disappear. Materials are constantly changing due to the intense price competition in the industry.

It is precisely because of these points, that your chances of linking a suspect to a crime scene, using duct tape as evidence, can be much more than merely coincidental. There is enough variation within the products and the process to support the notion that two reasonably matched samples could likely come from the same source.

Construction

Duct tape consists essentially of three components — a film backing, a fabric reinforcement, and the adhesive (Figure 1). There are probably two or three dozen basic models of duct tape in which the amount and

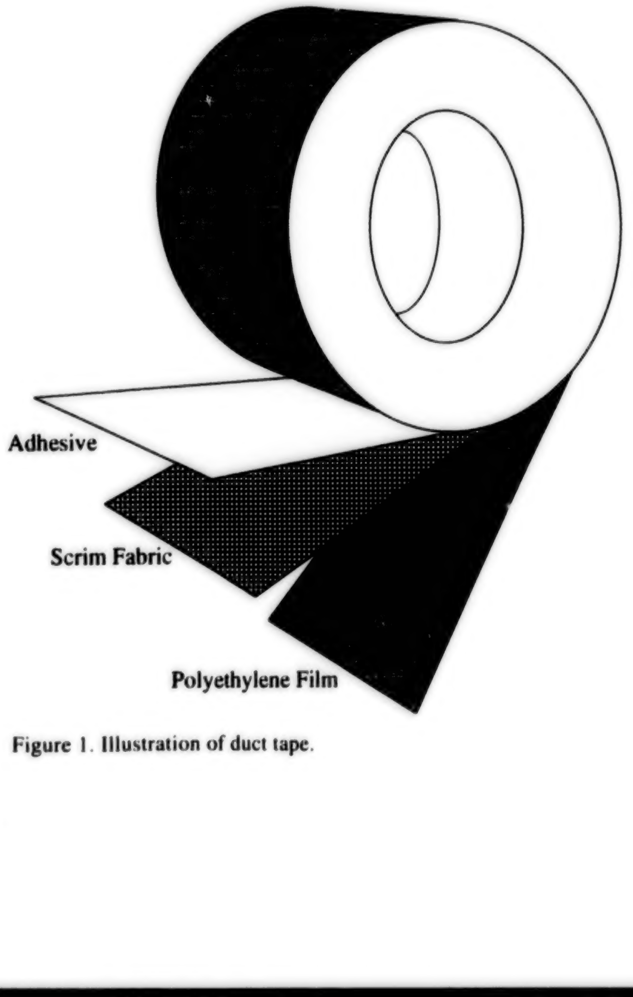

Figure 1. Illustration of duct tape.

quality of each component is varied to meet the needs of a particular end use or market. The specific grade of product can be a good clue to a suspect's profession or place of employment, since the various products are sold thru different distribution channels.

FILM

The film used as duct tape backing is typically a low density polyethylene blown film (Table 1). Other olefin polymers, such as linear low density polyethylene may be included to increase the strength of the film. For the standard duct tapes, the film is combined with the fabric and adhesive via a high pressure laminating process referred to as calendering.

The film may range in thickness from as little as 1.5 mils to more than 4 mils. Product cost and appearance and, to a lesser degree, functionality determine the thickness of the film that is used. Thin films show the fabric pattern most visibly, and are used in the low end commodity and retail products. Thicker films show less of the fabric pattern and may completely mask it. Those tapes are used more by craftsmen and in more demanding industrial applications.

A colorant is included in the film to provide the tape its color. Aluminum metal powder is used for the typical silver grey color. Duct tape can be made in virtually any color, though black, white, red, yellow, and olive drab are the most common. The film may be vacuum metalized to provide a bright silvery appearance.

Shuford offers twelve standard off the shelf colors, including Richard Petty blue and Daryl Waltrip orange. Custom colors are available for a 500 case minimum order (3600) rolls. We have made purple colored tape for one customer who wanted to reduce the theft of tape from his job sites.

Other additives, such as flame retardants, may be included in the film for functional purposes. The film may be printed. The state of California requires the manufacturer's name and product number on all tapes used in permanent applications in the construction industry. The film may also be embossed.

There are several products related to duct tape in which the polyethylene is applied as a molten material during the calendering operation rather than a preformed film. Kendall Corp. has a patent on this process and manufactures these tapes with and without fabric for pipe wrapping and asbestos removal.

The polyethylene may be applied via extrusion coating, to a high count, thin fabric. These tapes are produced primarily in Japan and Korea and usually made with rayon and a synthetic rubber adhesive.

Finally, there are dull, matte finished tapes of various colors, that are used in the motion picture and entertainment industries because they don't reflect light. These tapes are made with a polyvinylchloride plastisol coating applied to a high count cotton fabric and are called gaffers tape.

Table 1. DUCT TAPE FILM BACKING

Thickness
- < 2 mills — low end commodity, retail
- >2 mills — craftsman, industrial

Low density polyethylene (LDPE)
Linear low density polyethylene (LLDPE)

Aluminum powder — silver/grey color

FABRIC

The fabric used in duct tape is typically a low count, woven scrim or gauze cloth (Table 2). In the past, this cloth was all cotton. Currently, polyester cotton blends are used. The polyester is less expensive and provides better strength and elasticity, yielding a fabric that is thinner and has good stability. The cotton allows the tape to be torn by hand. Blend levels range from 50/50 to 65/35.

Duct tape fabrics are described by the term yarn count, which is the number of yarn ends per inch in the warp, or machine direction, followed by the number of ends in the filling direction. Yarn counts range from the very low end 20 X 8 to the high end 54 X 28. The high count fabric would contain more than three times the amount of yard of the low count fabric.

As with the film, product cost, appearance and functionality determine the fabric that is used in a specific tape. At present, 20 count fabrics are predominant in retail grade tapes and those with counts of 30+ are used industrial tapes. A mid range 24 count fabric is found in both markets as either a high end retail tape of a cheap contractor grade tape.

Table 2. DUCT TAPE (SCRIM) FABRIC

Warp Yarns — machine direction (MD)
- Strength of tape determined by the number of yarns, size, and type
- Ease of tearing determined by polyester/cotton blend ratio

Filling Yarns — cross direction (CD)
- Type and number determines the stability, appearance and bulk of the tape

Yarn Count — warp X fill - ends per inch
- 20 X 10 — low end commodity, retail
- 24 X 16 — craftsmen, painting and HVAC
- 38 X 24 — industrial, specification grade

The fabrics are used in their greige or unfinished state. Process aides, such as starch or polyvinyl acetate, used in weaving the fabric will be found on the warp yarns. Much of the yarn used for duct tape fabric is second quality apparel yarn which may not accept dye properly or may not resist shrinkage. Optical brighteners may be present in those yarns. In rare cases, the yarns may be treated with a flame retardant or may be dyed.

Particular yarns are used by specific tape producers. Kendall Corp. has a patent on the use of texturized filling yarns to add bulk and thickness to the tape. Shuford uses spun filament yarns to avoid that patent. Japanese and Korean tapes use rayon due to its availability. There is presently no domestic source for rayon. Acrylic yarn was used in the past, but that is also no longer available. Virtually all duct tape fabric is now woven. A knit construction that was popular in the early eighties lost out economically to the newer high speed air jet looms.

ADHESIVE

The adhesives used on duct tape are generally natural rubber compounds which contain tackifying resins that provide the "stick-um" and inert fillers that add bulk (Table 3). The natural rubber is imported from Malaysia, Indoesia, and Liberia, and is available in a variety of grades of purity and quality. Natural rubber is traded as a commodity and its price can change dramatically due to supply and demand or pure speculation. Reclaimed or reprocessed natural rubber is often used in addition to or as a replacement for virgin rubber based on price and the tape producer's manufacturing process. Synthetic polyisoprene was used several years ago when the AIDS scare led speculators to double the price of natural rubber for a short period of time. Other rubber polymers such as styrene-butadiene, styrene-isoprene, and butyl rubber may be used, though generally as minor components, for functional or economic reasons.

Table 3. DUCT TAPE ADHESIVE

RUBBER	Natural Rubber (NR) Synthetic Polyisoprene (SIR) Reclaimed, Reprocessed Rubber
RESIN	Aliphatic (C5) Hydrocarbon Natural Rosin Ester
FILLER	Clay, Kaolin, Aluminum Silicate Calcium Carbonate
OTHER COMPONENTS	SBR, SIS, Butyl Rubbers Aromatic, Terpene, Phenolic Resins Titanium Dioxide Zinc Oxide Extender Oils, Polybutene Antioxidant Process Aides Flame Retardants

Tackifying resins solvate the rubber and make it sticky. These resins are low molecular weight polymers derived from by-products of several chemical process industries. Aliphatic hydrocarbon resins are produced from the "C5" fraction that is a by-product of petroleum refining and ethylene production. The natural rosin tackifiers are produced from by-products of paper manufacturing. Some resins contain both types of monomer. Other resins contain additional monomers such as "C9" aromatics and acid functional groups.

There are several dozen varieties of tackifying resins available from more than ten different manufacturers. The resins are classified by melting point and range from 10°C to 100+°C products. Most adhesive formulations contain at least one low melt and one high melt resin. The types and amounts of resin used represent the black art of adhesive formulation. Choice depends on the rubber used, performance properties that are required, the formulator's whims, and or course, cost.

Inorganic fillers are added to the adhesive to increase bulk and allow for the thick adhesive coating that is applied on duct tape. Aluminum silicate (clay) and calcium carbonate are the most common. Choice is based on price and proximity to the source, since packaging and shipping may be more than the cost of the filler.

Other components may be present in minor amounts in duct tape adhesives for various specific purposes. Titanium dioxide is used to opaque and pigment the adhesive white in color. Consumers often perceive a white adhesive as purer and better in quality. Phenolic resins, used along with zinc oxide, provide chemical crosslinking which improves the shear strength and holding power of the adhesive. Industrial grade duct tapes are crosslinked to limit adhesive flow. Extender oils and polybutene resins plasticize the adhesive and improve quick stick properties. Antioxidants protect the adhesive from degradation during processing and extend the shelf life of the tape. Process aides reduce the time cycle required to mix a batch of adhesive. Flame retardants are required in tapes used in aircraft and some construction industries.

PROCESS

The duct tape manufacturing process will be hard for me to describe in words and difficult for you to visualize (Table 4). Traditional rubber processing equipment, such as that in the tire manufacturing industry, is utilized. The rubber is first masticated and broken down in a Banbury internal mixer using heat and high shear. The resins, fillers, and other ingredients are added to the

Table 4. MANUFACTURING PROCESS

Rubber	Banbury Internal Mixer
Resin & Filler	Two Roll Mixing Mill
Film & Fabric	Rubber Calender

Jumbo Roll (60 in. x 2000 yd.)
Slitting
User Roll (2 in. x 60 yd.)
Packing

rubber on a two roll mixing mill. The result is a sticky, gooey mass of adhesive that looks like bread dough. The adhesive is applied to the film and fabric backings using heat and very high pressures to form the laminated tape by means of a rubber calendar. That device is basically a set of three very large squeeze rolls, machined to a precise tolerance, that control the thickness of the adhesive that is applied. Jumbo rolls of tape that are four feet or more in width and two thousands yards in length are produced at speeds of seventy yards per minute or more. The jumbo rolls are cut into user sized rolls of tape on rotary shear knife slitter rewinders. The tape is then packaged for distribution and sale.

DUCT TAPE PRODUCERS

The three major producers of duct tape (Table 5) are: Shuford Mills Inc., Tape Division, Hickory, NC, whose plant is located in Stony Point, NC; Nashua Corp., Tape Division, Nashua, NH, whose plant is located in Watervliet, NY; and Kendall Corp., Polyken Division, Westwood, MA, whose plant is located in Franklin, KY. Other producers are Tesa Tuck Industries, New Rochelle, NY, with a plant in Middleton, NY; and Anchor Continental, Columbia, SC, whose plant is in Columbia.

Table 5. DUCT TAPE PRODUCERS

Company	Market Share (%)	Million sq. yds.
Shuford Mills; Hickory, NC	35.5	52.5
Nashua; Nashua, NH	31.7	46.9
Kendall-Polyken; Westwood, MA	23.0	34.0
Others Tesa Tuck Anchor		

According to industry surveys, the big three produced over 130 million square yards of duct tape, accounting for ninety two percent of the volume made in 1989. That would amount to at least 40 million rolls of duct tape.

Producers label tape with their own brand name and with private labels for several dozen distributors and retailers. The majors produce tape for other tape manufacturing companies and also sell jumbo rolls to convertors that only slit and package the tape. Unlabeled, blankcore tape, or that marked only with the roll size is made for small volume and low end resellers. Thus, though there may appear to be an infinite number of brands and producers, the industry is very concentrated, and the number of different products is really quite limited.

DISTINGUISHING CHARACTERISTICS

Each of the duct tape manufacturers product lines have common, often unique, features that are dictated by their equipment capabilities, technology base, raw material position, formulating philosophy, and marketing policies (Table 6).

Shuford Mills is fully integrated and captively produces both the film and the fabric that are used in its tape, allowing constructions to be optimized for performance and cost. The films are blends of low density and linear low density polyethylene that are 1.8 or 2.5 mils in thickness. In some products a tri-layer co-extruded film which contains high density polyethylene is used. Shuford fabrics use 100% polyester filament filling yarns along with blended polyester cotton warp yarns. The current yard counts are 20 x 10, 24 x 16, 38 x 24, and the yarn pattern is quite symmetrical and regular. Shuford adhe-

Table 6. DISTINGUISHING CHARACTERISTICS OF DUCT TAPES

SHUFORD

LD/LLDPE blends and/or coextruded 3 layer film — 1.8 and 2.5 mil thick

100% polyester filament filling yarns

Clay filled adhesive, aliphatic hydrocarbon resin, off white or colorless adhesive (retail)

NASHUA

Irregular weave patterns, "odd" yarn counts

Reclaimed rubber adhesive, grey colored, rubber particles

Modular metric width, 48mm = 2 inch

KENDALL

Thicker film backings, sometimes embossed and/or calendered

Texturized filling yards

Multiple rubber components, rosin ester resins, most adhesives grey or black colored sives are clay filled and use aliphatic hydrocarbon tackifyng resins. Retail grade adhesives are off-white or colorless and certain industrial adhesives are gray in color.

Nashua tape typically has odd yard counts (19 x 20, 23 x 12) with very irregular weave patterns. Due to equipment limitations, their adhesives are believed to be made entirely from reclaimed rubber. All are gray in color and often show small particles of undissolved rubber. Nashua is the only producer to slit duct tape in the so called modular metric sizes. A two inch wide roll of Nashua tape will actually measure 48mm rather 50.6mm.

Kendall, formerly a division of the Colgate-Palmolive Corp., has the most sophisticated technology, and perhaps the most complex products. Their film backings are thicker and sometimes embossed. Texturized filling yards are used to give the tape greater thickness. Their adhesives often contain multiple rubber components and several types of resin. Most Kendall adhesives are gray or black in color.

ANALYSIS OF DUCT TAPE

With all of this in mind, what then should one look for in a piece of duct tape found at the scene of a crime? (Table 7) Simple appearance and basic physical measurements can reveal quite a bit. The color of the adhesive and the weave pattern of the yarn may indicate the probable manufacturer of the tape. For example, if the adhesive is off-white in color and the yarn pattern is symmetrical and regular, there is a good change that the tape produced by Shuford for the retail marketplace. Measurement of the yard count (that is), the number of yarn ends per inch in both directions, and the total thickness of the tape can reveal the relative quality. Thin tape with a low yarn count is typical of low end, mass market, retail products. Thicker tapes with higher yarn counts are more likely to be sold through professional and industrial outlets. The adhesive can be removed from the backing with toluene solvent or gasoline to allow measurement of the film thickness and adhesive weight applied per unit area.

High powered microscopy can be very useful in finger printing the fabric. It can reveal the fiber type and blend. Pyrolysis can be used to determine the total inorganic content of the tape and the amount of filler in the adhesive. Analysis of the adhesive is more difficult and will require some type of sophisticated instrumentation. Infrared spectroscopy can finger print the organic compounds. Flame ionization photometry and X-ray diffraction can identify the inorganic components.

Table 7. DUCT TAPE ANALYSIS

APPEARANCE

Color of adhesive and film backing
Texture and yarn pattern

PHYSICAL MEASUREMENT

Yarn count
Total thickness
Film backing thickness
Adhesive weight per unit area

MICROSCOPY

Fiber cross section

BULK ANALYSIS

Adhesive percent ash

INSTRUMENTAL METHODS

Infra-red spectroscopy
Flame ionization
X-ray diffraction

Duct tape found at a crime scene can usually be removed using patience and some heat from a hot air blower such as a hair dryer to soften and cause the adhesive to flow. Alternately, a freon spray can be used to embrittle the adhesive and cause it to lose its adhesion. Tape samples are most easily preserved by winding the tape on its own backing as it was in the original roll of tape.

Though all duct tape may appear to be the same to a casual observer, that is really not the case. It may be a key piece of evidence for linking a suspect to a crime scene, or for a search warrant of a possible suspect's home or car. Often, it may be stolen by the criminal from his place of employment and may reveal his trade or profession. Probably, not much thought is given to the tape that is used, and thus little may be done to conceal any tape that remains. Duct tape has played an important role in several criminal cases that I know of, and I answer regular calls from various law enforcement agencies on a regular basis. Unfortunately, our great "All American" invention has fallen into perverse uses that were never intended.

ACKNOWLEDGMENTS

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SOIL IN TRACE EVIDENCE ANALYSIS

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The use of soils as trace evidence has existed for approximately one hundred years. It began as so many of the other types of evidence with the writings of Sir Arthur Conan Doyle. Doyle wrote the Sherlock Holmes series between 1887 and 1893 (Doyle 1956). He was a physician who apparently had two motives: writing salable literature and using his scientific expertise to encourage the use of science as evidence.

In 1893 Hans Gross wrote his book, "Handbook for Examining Magistrates," in which he suggested that perhaps you could tell more about where someone had last been from the dirt on their shoes than you could from toilsome inquiries. Yet the first actual case was done by a German chemist, Georg Popp, in Frankfort in 1904.

Popp is most famous for the Margarethe Filbert case in 1908. In this murder a suspect had been identified by many of his neighbors and friends because he was known to be a poacher. The suspect's wife testified that she had dutifully cleaned his dress shoes the day before the crime. Those shoes had three layers of soil adhering to the leather in front of the heel. Popp, using the methods available at that time, said that the uppermost layer, thus the oldest, contained goose droppings and other earth materials that compared with samples in the walk outside the suspect's home. The second layer contained red sandstone fragments and other particles that compared with samples from the scene where the body had been found. The lowest layer and, thus the youngest, contained brick, coal dust, cement and a whole series of other materials that compared with samples from a scene outside a castle where the suspect's gun and clothing had been found. The suspect said that he had walked only in his fields on the day of the crime and those fields were underlain by a porphyry with milky quartz. Popp found no such material on the shoe although the soil had been wet on that day. In this case, Popp had developed most of the elements that we deal with today in a soil examination. He had compared two sets of samples and identified them with two of the scenes from the crime. He had confirmed a sequence of events consistent with the theory of the crime and he had offered no contribution for supporting the alibi.

Studies such as these provided the foundation for the science of forensic geology, as we know it today. The common use of soil examination began with the pioneering work of the French criminalist, Edmond Locard, in the years following 1910. He provided us with a statement of the well-recognized transfer principle.

A chapter titled "History - Sherlock Holmes to the Present" appears in a book on forensic geology by Murray and Tedrow (1992) and discusses the contributions of the previously mentioned scientists, Gross, Popp and Locard.

We believe soils have evidential value. This belief lies in the almost unlimited number of kinds of soil and the large number of measurements that we can make on these materials. For example, the number of sizes and size distributions of sand combined with colors and shapes and mineralogy is almost unlimited. Every elementary geology student who has had to learn even the common minerals for an exam knows there are many and in this vastness lies the evidential value. In rock types alone, for example, there is an almost unlimited number of kinds of granite. These are identifiable and recognizable. They differ in color, mineralogy, texture, and all those other characteristics that you can use in identification. There are over a million different kinds of fossils and fossils assemblages. It is this diversity in earth materials, combined with the ability to measure and observe the different kinds, that gives us our discriminating power.

Soil is produced by an almost unlimited number of processes that, through the course of millions of years, have deposited and modified different types of soils in different places. Soils do not change linearly; they change abruptly and one kind may have no relation to the next, even in a small area. For this reason, it is doubtful if the type of statistical information that is available for the various types of man-made evidence will be developed for soils in the immediate future.

We have seen many contributions to the discipline over the last 100 years and leaders in the field recognize the contributions made by the Federal Bureau of Investigation Laboratory. In addition, significant contributions have been made over the past thirty years by the Central Research Establishment in the United Kingdom and McCrone Associates in Illinois.

Like statistical information, methods for examining soils as trace evidence are difficult to standardize. Because of the diversity of material, we sometimes must change methods in order to get the maximum evidential value. The binocular microscope provides an important first-step examination. The microscope represents a powerful tool because the evidential value of soils lies in the diversity and the differences in the minerals. Methods that combine general properties, such as the density gradient column, do not take advantage of this diversity. This method not only has problems in reproducing the analysis, but provides the same observation on two totally different minerals simply because they happen to have the same density. We have seen far less use of this method in the last few years. Murray and Tedrow (1975) questioned the method and, Chamberlain and Howarth (1983) provided evidence on the method's very limited value. Murray and Tedrow (1992) summarized the inherent problems with the density gradient column and similar types of examination.

In the forensic use of soils, identification alone is seldom useful. There have been cases where the identification of safe insulation on the person or property of someone not engaged in the legitimate manufacturer or repair of safes has at least been probable cause for further investigation. In terms of individualization, that certainly is not possible in most of the cases we see. For example, someone took a concrete block, smashed it into pieces and caused considerable damage throwing those pieces through drug store windows in southern New Jersey. The pieces were collected and put back together with those pieces found in the back of the suspect's truck to form the original block. Another example was a rape case in which the knee impressions of the individual were found. Soil on the left knee of the suspect compared with the sample from the left knee impression. Soil on the right knee compared with the sample from the right knee impression and a geologic contact between two significantly different soil types separated the two impressions. Such evidence provides a very high level of confidence; however, individualization in the sense that we normally think about it probably does not exist.

One of the most interesting types of studies is the aid to an investigation. The Toronto liquor store dealer was rather unpleasantly surprised to open a carton of whiskey and find neatly chiseled little blocks of rock in each of the slots rather than expensive Scotch whiskey. Cartons with similar substitutions appeared in other places, such as Boreno. In this case, identification of the source becomes the real lead to the investigation. The rocks were identifiable and, because they were clean and neatly chiseled, probably came from a quarry. Using geologic maps, the location could be narrowed, the quarries examined, and the investigation ultimately led to the conviction of a man at a packaging plant who had a nearby quarry and enjoyed chiseling rocks.

In a similar case, an exhumed, unembalmed body in a green plastic garbage bag was left at the police pistol range in Linden, New Jersey. There really was no other evidence, other than the soil mixed with that body. Examination of the soil revealed that it was dredgings from Newark Bay which are used to produce new land from fill. This information ultimately led to the identification and conviction of a mother and daughter who murdered the father and buried him underneath the front porch of their new home in a subdivision on made land.

Most examinations involve comparison. Comparison is establishing a high probability that two samples have a common source. In comparison studies of soils, it is difficult to overestimate the value of findings in the soil artifacts or some other type of evidence. The use of the microscope with soils is especially valuable because of the possibility of finding other particles. A very interesting case in California, reported by the California Division of Mines and Geology, illustrates this value. A man by the name of Stanley was convicted of murdering his second wife in 1975, imprisoned, and after four years he was released. In 1980 he was convicted of murdering his fourth wife. But the day before Stanley murdered her, he was gracious enough to pick up a young lady and give her a ride. She too was murdered and her body was dropped at an oil well apron made of gravel. Found in the suspect's car was soil material that partially compared with local material from around the oil well, but not completely. There were other fragments that did not compare. Further investigation led to the fact that the oil company had bought some gravel 300 miles to the south and spread some of it around that oil well apron. When the combined sample of the local material and the imported material were compared with that found on the floor board of Stanley's vehicle, it produced an excellent comparison. This illustrates the importance of the unusual, the artifact, and of finding some other bit of trace evidence.

In some cases soil is the only physical evidence. Larceny of cactus is big business in Arizona. A friendly landowner provides a bill of sale and the big cactus are removed from federal property. Once the plants are on a highway, only the soil on the roots can testify to the original growth location.

Similarly, in an Upper Michigan rape case, three flower pots had been tipped over and spilled on the floor in the struggle. It was shown that potting soil on the suspect's shoe compared with one of those flower pot spillings. In addition, small clippings of blue thread existed both in that flower pot sample and on the shoe of the suspect. Again, the examination of the soil provided additional trace evidence.

In a another rape case in New Jersey, the location was a vacant lot in back of a bar. The suspect had soil samples in the cuffs of his pants which were typical glacial sand of northern New Jersey. In addition, the soil contained fragments of clean Pennsylvania anthracite coal. Such coal fragments are not uncommon in most of the older cities of the east. In this sample there was too much coal when compared with samples in the surrounding area. Further investigation showed that some 60 years ago, the vacant lot in back of the bar was the coal pile of a coal burning laundry. Again, the tying in of soil evidence with an artifact and history increased its evidential value.

The alertness of those who collect samples, and the quality of collection, is critical to the success of any examination. For example, there is the case in which an alert police officer happened to look at an individual arrested on a minor crime. He observed "that's the worst case of dandruff I have ever seen." It was not dandruff but diatomaceous earth, that compared species to species with the insulating material of a safe that had been ripped the previous day.

A recent case illustrates a lesson on the importance of knowing the history of the sample. In an armed robbery in Montana, the individual wore a ski mask. Soil samples collected from the ski mask and from the place where the individual had fallen and picked up soil on the mask compared in terms of size, color and mineralogy. The comparison was excellent with the exception that the sample from the ski mask contained many small glass beads. The problem was solved when the actual examination of the ski mask revealed that it had a strip of reflector tape, containing the glass beads, and that they had been incorporated in the sample removed by the evidence technicians from the mask.

When we consider the future of soil examination, several observations can be made: new methods are being developed to take advantage of the discriminating power inherent in earth materials; and quantitative x-ray diffraction may possibly revolutionize soil examination. When developed to the point that it becomes an ordinary lab technique, the ability to take a soil sample and do a quantitative x-ray determination will provide an easy reproducible identification of those factors that have the discriminating power. As you well know, this is not now possible, but tremendous advances are being made in that direction.

Considerable effort must also be devoted to our finding appropriate sampling methods and training those people who collect samples. We have all seen the case where 30 soil samples arrive that have been systematically collected. Because of the discriminating power inherent in soils, they are extremely sensitive to change over short distances, both horizontally and vertically. Soil sampling in many cases is the search for a sample that compares. The collecting of all the other samples serves only the purpose of demonstrating the range of local differences. In collecting soil samples for comparison, we are searching for one that would have the possibility of comparison and, therefore, screening techniques during sampling that eliminate samples that have no relation is appropriate. For example, a surface sample offers little possibility when comparisons are to be made with materials from a depth of five feet in a grave.

There is a classic example of soil from the back bumper of a vehicle. The vehicle had actually backed down into a burrow pit that had been cut back by a grader. The only possibility of comparison was at a layer some three and a half feet below the surface because the bumper hit that depth in the burrow pit. However, dozens of samples were collected at the surface.

There is a tremendous need for studies that attempt to demonstrate the diversity of soils. One approach is to take an area that one would normally assume was fairly homogenous in its soil character and collect a hundred samples on a grid. Each pair of samples would then be compared with each other until all the pairs are shown to be different. Starting with color and moving on to size distribution and mineralogy, different methods are used to eliminate all of these pairs as appearing similar. Such studies serve several purposes. They provide a base of experience for believing that soils are unique to very small areas. They provide a body of information that you can use in demonstrating the evidential value of soils and the discriminating power of each analytical method.

The qualifications of examiners is a very major problem. How do you learn to do soil examination? This requires a thorough knowledge of mineralogy and the ability to effectively use a microscope and the other techniques used in soil examination. One of the problems that will continue to plague us in the future is that we now have techniques that are in a sense too powerful. The scanning electron microscope lets us look at a single quartz grain and we recognize intuitively that every quartz grain is different when examined at a high enough magnification. If every quartz grain is different, then the concept of comparison disappears. There is no such thing as comparison and the demonstration of common source. The choice of methods and the all important interpretation becomes the issue for the examiner and expert witness.

The value of soil evidence will increase. However, that increase will be determined by proper training of examiners and evidence collectors. Most important will be the development of more reliable and easy to use instruments combined with sound professional interpretation of the data.

REFERENCES

Chamberlain, K. and Howarth, P. S. (1983). Soil comparison by the density gradient method--a review and evaluation, Foren. Sci. Intern. 23:161-177.

Doyle, A. C. (1956). The Complete Sherlock Holmes, Vol. 1, Doubleday and Company, Inc., NY.

Murray, R. C. and Tedrow, J. C. F. (1975). Forensic Geology: Earth Sciences and Criminal Investigation. Rutgers University Press, New Brunswick, NJ.

Murray, R. C. and Tedrow, J. F. C. (1992). Forensic Geology, Prentice Hall, Englewood Cliffs, NJ.

FORENSIC GLASS COMPARISONS

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The 1980's have been witness to changes in the technology and philosophy associated with forensic glass comparisons. There has been extensive literature published in this area addressing all facets of these changes. This was the decade where the classification of small glass fragments was investigated. The interference objective could distinguish flat and curved surfaces, annealing methodology using a programmable mini-tube furnace could reliably differentiate glass particles from toughened or non-toughened sources, and where chemical analysis, using a variety of techniques (ICP-AES, SEM/EDX, XRF, INNA), was investigated as a means of predicting whether small particles originated from a container or source of flat glass. The measurement of dispersion lost popularity and the probative value of density and refractive index measurements was reassessed. The calculating digital density meter had been recently introduced and a semi-automated technique for the measurement of refractive index data (GRIM) grew in popularity and use. Perhaps the largest impact in forensic glass comparisons originated from the high degree of computerization readily available. Computer-driven instrumentation and laboratory automation systems allowed the manipulation and interpretation of complex analytical data and personal computers encouraged the creation of glass data bases. A direct result of the capacity for computerization was the requirement for a statistical interpretation of the data that was generated, whether instrumentally or as a result of the information captured on data bases. This need for an appreciation of statistics as applied to data bases generated interest in pursuing glass particle transfer and persistence studies and the investigation of the backward fragmentation of glass. Improved technology was the impetus for re-investigation of both intra and inter-source variations of different types of glass in an attempt to answer some of the statistical questions that were raised.

In addition to addressing these scientific issues, the Canadian forensic scientist also had to respond to changes in the legal system regarding Charter of Rights arguments which allowed defence council equal access to forensic trace evidence for independent assessment, and legislation on the acceptance of forensic evidence resulting from new technology. These legal changes have directly impacted the accepted practices and procedures employed in casework, particularly with respect to the preservation of evidence. The forensic scientist also perceives the need for standardized methodology and quality assurance as evidenced by the movement towards accreditation of laboratories and individual certification.

A complete explanation of forensic glass comparisons is beyond the scope of this text. The intent is to briefly review the basic concepts associated with forensic glass comparisons, describe the techniques used in Canada and highlight major trends or advancements in the discipline.

REVIEW

The American Society of Testing Materials definition of glass is, "An inorganic product of fusion which has cooled to a rigid condition without crystallizing". Glass has an amorphous liquid-like internal structure, commonly based on the silicon tetrahedron. It is hard and brittle, colorless or colored, and normally transparent. Glass is isotropic (that is, has a single refractive index regardless of the direction of light passing through it) and remains dark when viewed under crossed polars. Glass suffers conchoidal fracture.

The composition of glass types and glass manufacture have been dealt with extensively in the literature (Uhlmann and Kreidl 1984; Saferstein 1982) and will not be repeated here. This knowledge, however, is essential to the interpretation of data resulting from forensic glass comparisons and in the development of new techniques for glass analysis. For example, knowing that magnesium oxide is added to flat glass formulations to increase flow properties may allow the discrimination between flat glass and container glass. Rolled plate glass has a higher calcium oxide content than drawn sheet or float glass. The float process was first introduced in 1962 and now dominates flat glass production. The float (tin-contact) surface of this glass fluoresces under short-wave (254nm) ultra-violet light. Tempered glass is produced by the rapid cooling of glass at its surfaces resulting in a surface compression with the bulk of the glass existing in tension. Breakage characteristically results in cubic or diced fragments.

Refractive index variations for this type of glass can be considerable (0.00016) and inter-source variations for this type of glass must be considered when interpreting refractive index data in comparison situations. Likewise, formed or molded glass products such as headlamps also show a large variation in refractive index within a single source. These few examples illustrate the need for a solid understanding of glass manufacture.

Most of the glass encountered in casework in the RCMP forensic laboratories across Canada originate from flat glass sources. There are only three primary flat glass plants in Canada - AFG Glass in Scarborough, Ontario, Canadian Pittsburgh Glass in Owen Sound, Ontario and Glaverbel in Quebec City, Quebec. There is only one primary bottle glass manufacturer - Consumers Packaging (formerly Domglass and Consumers Glass), with several plants across the country. Domestically produced glass may tend towards uniformity in the properties measured such as refractive index and chemical composition. The importation of glass from other countries also has to be considered as part of the glass population, particularly when frequency histograms are used as an interpretive tool. For example, more glass from Japan would be expected to be found in the geographic area serviced by the Vancouver forensic laboratory than in areas serviced by other Canadian forensic laboratories. The refractive index distribution of glass from this geographic area may be different than that for Ontario where domestic sources of flat glass are readily available.

Glass, as trace evidence, has probative value that can link a suspect to a crime scene. The transfer of small glass fragments to a suspect can be accomplished as a result of actual contact (crawling through a broken window or carrying a TV covered with broken glass fragments) or by a phenomenon known as backward fragmentation. Here small fragments of glass are projected in a direction opposite to the direction of impact. This process has attracted much study and will be covered in more detail in the next section.

Refractive index determinations provide the cornerstone for forensic glass comparisons. It is a very precise technique that easily accommodates casework-size samples (normally less than 1 mm in their maximum dimension), it is non-destructive and has been proven to be very effective in discriminating glass from different sources. Refraction results when light changes speed and direction upon passing obliquely from one medium to another and refractive index is the numerical value that describes the extent of refraction. As such, refractive index can also be practically defined as the ratio of the speed of a wavelength of light in air to its speed in glass. The glass being more dense, generally acts to slow down the light such that bending occurs toward the normal. Each wavelength of light is bent by the glass to different extents such that if white light were to strike a prism obliquely, its wavelengths would be dispersed by the glass into their separate colors and generate a rainbow effect. Dispersion is a measure of the variation of refractive index with wavelength and can be expressed mathematically by the following expression

$$V = \frac{(n_D - 1)}{n_F - n_c}$$

Where V = dispersion
n_D = refractive index at 589nm (yellow)
n_F = refractive index at 486nm (blue)
n_c = refractive index at 656nm (red)

The possibility of a mechanical fit (physical match) must never be overlooked when the fractured glass particles are large. Tempered glass cubes are not appropriate for physical matching.

BACKWARD FRAGMENTATION

Small glass fragments recovered from the clothing of an individual can associate that individual to a crime scene involving the breaking of glass. An individual who is in close proximity to a source of glass as it breaks will be showered with glass fragments by a process commonly referred to as backward fragmentation. This phenomenon was first documented by Nelson and Revell (1967). Upon impact, glass distorts away from the force until the surface under tensile stress (opposite the force) ruptures. Cracks travel through the glass to the surface sustaining the blow and the compressive forces along the broken edges cause the glass to fracture in flakes and be projected in a direction opposite to impact. The distance these particles travel and the number of particles generated depended on the force of the blow, although in all cases, small fragments were found at least one m from the window (Nelson and Revell 1967). Particles were also reported to be found up to 3.5 m from the broken window. Most of the glass particles generated were described as flakes (beeswing) though the thicker plate glass panes also produced needle-like slivers of glass when fractured. Locke *et al.* (1985) report that tens of thousands of glass particles of casework size, are generated upon the disintegration of a toughened windscreen. These fragments are described as being chunky rather than as flakes, with surface fragments being wedge-shaped. Equal numbers of bulk and surface fragments were reported.

Pounds and Smalldon (1978) broke windows of various sizes with subjects at varying distances from the breaking glass. There, studies showed that the number of particles > 1mm found on an individual was similar to the number found on 300 cm^2 of the floor where the subject was standing. Persistence studies showed that very few fragments larger than 1 mm were retained, the number of glass fragments recovered from an individual decreased with activity, and hair combings may be valuable sources of glass evidence. He also suggests that glass found in pockets has a lower evidential value because of higher persistence.

Recently there have been two CRSE reports on the breaking of flat glass (Locke and Unikowski 1989a,b).

An experiment to study the breaking of 8 panes of 4 mm glass having dimensions of $1m^2$ showed that the majority of large fragments (5-1 mm) fall directly in front of the broken window, whereas smaller fragments (0.5-0.25 mm) fall more uniformly over an area described by a 180° arc. The number of particles decreases rapidly with the distance from the broken window. Part 2 of this study showed that variations in pane thickness, pane size and pane type (plain, patterned, wire-reinforced) gave approximately the same particle distribution on breaking, though the thicker (10 mm) panes tended to generate twice as many glass fragments as a comparable 4 mm pane. When the distribution of surface particles from glass panes and toughened windscreens was examined, 50% of particles 1.0-0.25 mm in size were surface particles, though the surface area may represent only a small proportion of the glass fragment. Most of the surface fragments originated from the front of the pane.

An internal RCMP report also studied the phenomenon of backward fragmentation and the transfer of glass fragments (Luce *et al.* 1991). General findings are in agreement with those previously mentioned. Most of the glass particles (90%) were 0.85-0.15 mm in size (typical of casework fragments). The majority of glass fragments recovered from the clothing of a bystander originated from the upper body garments, most of which represents surface glass. Bulk glass is more concentrated on the lower part of the body (pants and footwear). Again, the larger the fragment, the greater the probability of finding a flat surface. For float glass panes, knowing the relative position of the float surface to the suspect, may contribute to the evaluation of the forensic evidence. This concept is supported by Zoro (1983) who investigated the backward fragmentation of float glass. Float surfaces as small as $0.05mm^2$ on glass fragments as small as 18µg can be reliably detected by fluorescence spectrometry (Lloyd 1981).

The observation of tramlines when generating refractive index data is also very characteristic of the presence of surface fragments (Underhill 1980). At the match temperature of the bulk glass, tramlines from the float surface will appear as dark bands whereas the tramlines resulting from the non-float surface appear bright since the match temperature of the non-float surface has a significantly (≈5°) higher match temperature than the bulk glass. Similarly, at the match temperature of the bulk glass, some fragments may appear dark. These fragments represent float surface fragments, with the float surface presented to the observer.

The interference objective can also be used for the detection of flat or curved surfaces (Locke and Elliott 1984). Such information would be helpful in distinguishing container from flat glass as well as identifying surface particles for fluorescence determinations.

ANALYTICAL METHODS

I - Refractive Index Determinations

The determination of refractive index values for glass fragments has evolved through several phases. The Abbé refractometer, which required large samples having two flat surfaces and hopefully a perpendicular edge, gave refractive index data accurate to three decimal places. Dispersion staining using a dispersion staining objective, hot stage and controller, involved the subjective assessment of the color at the glass-liquid boundary for a preset temperature and subsequent color reading in order to determine the wavelength of the match. Dispersion colors result as a combination of refraction and reflection effects at the particle-liquid boundary when close to the refractive index match for one wavelength. Refractive index results were precise to ±0.001 (Ojena and DeForest 1972). McCrone (1974) used a monochromator to measure the wavelength of light, and employed the Emmons double variation method for determining the refractive index of glass.

This method involved immersing a crushed glass sample in a Cargille liquid whose refractive index was known to be slightly higher than that of the glass. The refractive index of the liquid decreases with temperature. This preparation was placed in a hotstage and the temperature varied in increments. For each selected temperature, the wavelength of light was varied, by using a monochromator, until the glass disappeared from the field of view of the microscope (Becke line method), and the match point was established. A plot of temperature vs wavelength for these match points created a dispersion curve. McCrone (1974) reported on a precision of ±0.0001 for this technique but cautioned that some of the immersion liquids are only accurate to ±0.001 in known refractive index, so that absolute data might not be accurate. The Becke line is the bright line that borders an immersed glass fragment and arises from the diffraction between the glass and the liquid when their refractive indices are different. As the refractive index of the liquid approaches that of the glass, the edges of the glass become increasingly more difficult to see. Ojena and DeForest (1972) recommended the use of phase contrast microscopy to accentuate the Becke line contrast near the match temperature. A technique combining phase microscopy with the immersion method and temperature control of the hotstage to ±0.1°C allowed the measurement of refractive index with a precision ±0.00004.

Out of this very precise method of refractive index determination, evolved the GRIM (Glass Refractive Index Measurement), a semi-automated instrument developed by Foster and Freeman Ltd. for the UK Forensic Science Service (Locke and Underhill 1985; Locke 1985). Cargille liquids were abandoned in lieu of silicone oils as immersion liquids.

The silicone oils are more versatile in that they are more stable over a wider temperature range. A series of standard glasses of precisely known refractive indices were used to calibrate these oils. This calibration data is stored internally in the GRIM so that determination of a match temperature can directly generate the corresponding refractive index for the unknown glass.

The GRIM is composed of a transmitted light microscope equipped with phase contrast accessories, a video camera, a TV monitor, a control unit with a printer, a hotstage and a keyboard (Locke and Underhill 1985). A narrow band pass filter (≈589nm) with conventional illumination, is used to create the wavelength of light at the sodium D line, instead of a sodium arc lamp. A long working distance objective is essential for use with a hotstage. The match temperature of a glass fragment is determined by positioning the edge detection gate over a glass edge where the Becke line is bright (high contrast). The video signal from this gate is horizontally scanned as the temperature of the hotstage changes at 2°C/min. and the change in contrast of the Becke line is monitored through the match temperature. A match temperature for cooling and heating is established and a mean match temperature is calculated. This process eliminates the effects of temperature lag between the hotstage and the glass. Repeated measurements on a single edge resulted in a precision of ±0.02°C indicating high short term electronic stability for the instrument (Locke and Underhill 1985). These match temperatures are automatically printed when using the AUTO routine, along with an edge contrast value (0-99) that gives a measure of the quality of the edge chosen. A print function allows the operator to input relevant case information, accesses the appropriate calibration curve and automatically prints a refractive index for the experimentally determined match temperature of the unknown glass.

The GRIM has several advantages over the use of the Mettler hotstage and controller unit, though its performance is comparable (Locke and Underhill 1985). The GRIM provides an objective measure of match temperature, the match temperature is automatically converted into a refractive index value, the quality of the results can be assessed by examination of the edge contrast figures and the results are generated in hard copy. Most noteworthy, GRIM eliminates the operator fatigue associated with the visual assessment of match temperature using the Mettler technique. Long term stability of the GRIM is monitored with the calibration glasses over time, and a tolerance of ±2°C is set for the match temperatures. Constant deviations outside this limit require the generation of new calibration data. Calibration data is generally valid for years, indicating excellent long term stability. The precision of RI determinations using the GRIM is ±0.00001, a 0.1°C increase in temperature resulting in a change in RI of 0.00004. The homogeneity of refractive index for various types of glass can be investigated because of the precision of the technique.

The typical standard deviation associated with optical glass is 0.00002, whereas modern window glass has an average standard deviation in the order of 0.00004 and tempered glass, being more inhomogeneous due to its heat treatment, typically exhibits a standard deviation of 0.00016 (Locke 1985). The refractive index of a glass sample is dependant upon both its chemical composition and the manufacturing process that it has been subjected to. Variations in refractive index will be addressed in conjunction with the interpretation of the analytical results.

It is interesting to note that the measurement of dispersion has lost its popularity in recent years. Several authors have commented on its evidential value. Locke and Perryman (1985) examined the dispersion of 50 samples, comprising a collection of glass from diverse sources, using the GRIM and three narrow band pass filters corresponding to the F (blue), D (yellow) and C (red) lines. The total range of dispersion was 60 x 10^{-5}, which is narrow compared to the range in optical glasses (525 x 10^{-5}) whose chemical compositions are specially formulated to maximize dispersion differences. The standard deviation associated with dispersion was found to be 8 x 10^{-5}. Since four times the standard deviation is required for discrimination between samples, it was found that the vast majority of glass samples could not be discriminated by measuring dispersion when using the GRIM to generate refractive index data. It may be worthy to note that the response of the camera in the blue and red regions of the spectrum is not as sensitive as for the yellow region and that higher standard deviations in refractive index result when these two filters are used. Slater and Fong (1982) have also discounted the evidential value of dispersion over refractive index.

II - Density

Density is a physical property reflecting weight per unit volume. The density of glass has historically been used as a parameter in the discrimination of glass fragments, along with refractive index determinations and dispersion. Measurements of the density of glass particles have been accomplished through various sink-float methods involving the use of a pycnometer (Fong 1973), or thermally-induced density gradients (Greene and Burd 1965), displacement methods (Miller 1976) and weighing in air and water (Dabbs and Pearson 1972). Density determinations on known and unknown glass fragments in casework tended to be comparative only. These techniques are time consuming, require large sample sizes (≈5 mg - Dabbs and Pearson 1970) and are very sensitive to error resulting from those factors associated with the shape and condition of the glass particles, as well as small changes in temperature.

The Calculating Digital Density Meter was found to be effective in determining the density on smaller (0.1 - 0.2 mg) glass fragments (Beveridge and Semen 1979). The sink/float method is used, but rather than a density gradient, the suspension liquid is a homogeneous solution of bromoform (ρ^{25} 2.8875g/ml) and ethylene bromide and (ρ^{25} 2.1700g/ml). When a density match is made between the liquid and the glass, the instrument directly measures the density of the liquid electronically by monitoring the response of an oscillating u-tube to the liquid. Precision for the technique is quoted as 0.0001g/ml. Using glass density standards to calibrate the instrument, the range of each standard was 0.0003g/ml (Beveridge and Semen 1979). Density determinations of this type required 30-40 minutes per sample. Though smaller sample sizes could be accommodated, the precision of the technique remained at the same level reported earlier (Dabbs and Pearson 1970). Densities in the window glass range are typically 2.45 to 2.55 g/cc.

It is commonly accepted that there is a high correlation between density and refractive index. The Newton-Drude and Lorentz-Lorenz equations (Dabbs and Pearson 1972) are the best approximations to describe the relationship between refractive index and density for glass. However, it is obvious that the correlation does deviate from the predicted straight-line relationship when scattergrams of experimental data of these two parameters are examined (Stoney and Thornton 1985). Density and refractive index values vary with the composition of the glass. It is predicted that a change in calcium oxide content of 1% in a glass formulation could produce a refractive index change of 0.00300 (Locke and Hayes 1984). Density and refractive index are also a function of the thermal treatment of the glass, but to a lesser extent. Minor compositional differences and differences in the thermal history of glass samples could account for the non-ideal correlation of refractive index and density, so that density determinations of glass samples having the same refractive index could be useful in the discrimination of glass fragments from different sources.

Slater and Fong (1982) report on discrimination thresholds for refractive index and density. Using dispersion staining for refractive index determinations and a multiple tube comparator for density determinations (a sink/float method), they showed that density has a discriminating power six times that of refractive index. They also commented that "the discrimination threshold for refractive index must be in the order of 0.00015 (with a standard deviation of ±0.000025) before refractive index can be said to have a proof value equal to that of density". Using the GRIM for refractive index measurements allows these criterion to be met today.

Since refractive index determinations can be carried out quickly and reliably on small samples using the GRIM with a high level of precision, it continues to be the technique of choice in the comparison of glass fragments. Density may provide additional discrimination providing sufficient sample size permits, however the thermal histories of glass samples can be investigated by annealing and compositional differences may be investigated by other analytical methods.

III - Annealing

The fact that laboratory annealing of glass fragments could narrow the variations in the physical properties of glass fragments due to their thermal history, was reported in 1970 by Dabbs and Pearson. Their study involved the annealing of large samples and the measurement of the changes in density. The change in refractive index with annealing (ΔRI) has been studied to assess its evidential worth.

Annealing (controlled cooling) allows molecular packing to occur in the amorphous, open structure of glass and relieves the structural stresses in the glass imposed by manufacture. Generally, this results in an increase in refractive index and density. The RCMP laboratories currently use a Carbolite mini-tube furnace equipped with a Eurotherm controller/programmer to anneal small glass particles. The methodology used follows that described by Locke *et al.* (1985) with few variations - sample boat designs were modified to a depth of 1.5 mm from 3.0 mm to facilitate the transfer of small glass particles and the routine was shortened to 50 minutes.

Though large fragments of tempered glass can be identified by observation with polarized light (Sanger 1973), until recently this was not possible for small fragments. Locke *et al.* (1982) comment on the usefulness of annealing methodology to discriminate tempered from non-tempered glasses. The refractive index change upon laboratory annealing (ΔRI) is consistently higher for tempered glass sources than for non-tempered glass sources. This report indicates that above a RI threshold of 150 x 10^{-5}, glasses can be reliably predicted to have originated from a tempered source. Below this threshold value, the sources are non-tempered whether from containers, float or non-float windows. Ryland (1986) confirms the demarcation between tempered and non-tempered sources but reports a lower threshold value for ΔRI of 125 x 10^{-5}. Preliminary studies in this laboratory support these figures. The variation in refractive index of tempered glass sources before annealing (≈0.00016) is much reduced after annealing as the refractive indices approach a single value (Locke and Hayes 1984). Non-toughened glasses followed the same trend but to a lesser extent. Container glasses may not exhibit this tendency if refractive index variations are due to chemical inhomogeneity instead of structural stress, so that large variations in RI will exist before and after annealing. The values of RI for container glass covers a broad range that overlaps most of the non-tempered window glasses. Locke and Rocket (1985) report that just as tempered glass gives high ΔRI values, old kiln-annealed glass will give characteristically low values. In glasses showing a wide range of refractive indices that overlap, annealing may separate the mean RI's and cluster the results to allow discrimination (usually assessed at four times the associated standard deviation). For toughened glass as a whole, this discrimination value would be high (20 x 10^{-5}) and discrimination is expected to be poor within the group (Locke and Rockett 1985). Other discriminations between glass types (bottle glass vs laminated windshields) may be possible with further study (Marcouiller 1990). It is interesting to note that it may be possible to predict the thickness of a glass source from observation of the ΔRI of a small particle. Plots of log (thickness) vs ΔRI for various types of glass show a linear relationship (Winstanley and Rydeard 1985). It is obvious that considerable ΔRI data has to be generated before further trends can be identified.

IV - Chemical Composition

There have been many papers published in recent years addressing the chemical analysis of small glass fragments for discrimination and classification. Many techniques have been investigated in an attempt to identify the best elements for analysis to provide this discrimination, particularly between glass types. Hickman *et al.* (1983) analyzed glass fragments using neutron activation analysis (NAA), inductively coupled plasma-atomic emission spectrometry (ICP-AES), atomic emission spectrometry and atomic absorption spectrometry (AAS). The absolute concentration of 22 elements was determined for 49 samples of sheet, container and tableware glasses having refractive index values of 1.5177 to 1.5183. Magnesium was found to be the single most discriminating element. In a further study, Hickman (1983) used ICP-AES to study the concentration of Mn, Mg, Fe, Al, Sr and Ba in 232 samples of sheet glass. The determination of these six elements provided increased discrimination over RI measurements alone but gave poor discrimination for colorless float glasses of RI 1.517 - 1.519. Strontium was effective for discriminating between glasses having a low refractive index (<1.5165) whereas barium was able to provide discrimination of glasses having higher refractive indices.

The scanning electron microscope equipped with an energy dispersive X-ray spectrometer (SEM/EDX) has been used to study the chemical composition of glass. This technique is sensitive to 0.1%, fast and non-destructive. Reeve *et al.* (1976) used energy dispersive X-ray techniques to analyze 81 samples of glass including samples from successive production batches. Concentrations of Mg, Fe, Cu, Zn, As, Rb, Sr and Zr were ratioed against calcium. Only two samples were indistinguishable in these elements, and by combining other physical properties, all these samples were distinguishable from each other. Other authors report the use of SEM/EDX in glass analysis to provide discrimination using multi-element analysis on glasses from different countries (Terry *et al.* 1984), while Andrasko and Maehly (1978) and Ryland (1986) address the use of multiple techniques in the discrimination of glass. Keeley and Christofides (1978) compare analyses using X-ray microanalysis and the SEM and X-ray fluorescence (XRF). It is not possible to discriminate between sheet glass and container glass on the basis of magnesium content alone, though at first glance there seems to be a general separation of these two types based on an examination of the relative magnesium concentrations.

Energy dispersive X-ray fluorescence spectrometry is a technique that shows considerable potential in discriminating glass of different types having the same refractive index and is appropriate for glass fragments weighing between 2 mg and 100 μg (Howden *et al.* 1978). Further studies using this technique indicate that classification into window or non-window sources is also possible (Dudley *et al.* 1980). This technique is relatively fast, non-destructive and suitable for small samples (≈200 μg).

Koons *et al.* (1988) provide a comprehensive review of elemental techniques applied to glass analysis in their discussion of the best elements to use for classification. They analyzed 184 samples of colourless container and sheet glass (≈50 mg in size) by ICP-AES and determined the concentrations of Ba, Al, Ca, Fe, Mg, Mn, Na, Sr, and Ti. Effective classification of glass fragments is anticipated for fragments larger than 500 μg. Glass fragments from different sources, having the same optical properties, can be discriminated by an elemental analysis using ICP-AES. The technique, however, is destructive and thus requires relatively large sample sizes in order to conduct multiple examinations.

Pitts and Kratochvil (1991) used neutron activation analysis (INAA and CINAA) to study the chemical composition of glass samples that had been grouped according to their refractive index values. Sodium, aluminum and calcium counts were determined for sample sizes of 100 μg to 5 mg. Aluminum was found to be the best discriminating element followed by sodium then calcium. Analyses of float glass samples from two different Canadian manufacturers suggested that the aluminum content could be used to distinguish between them. Though this technique is non-destructive, the equipment is specialized and analysis times remain long in comparison to other, more versatile analytical techniques. The RCMP laboratories are currently evaluating suitable techniques for the elemental analysis of small glass fragments.

INTERPRETATION OF RESULTS

I - Variations in Properties

Prior to assessing experimental data in order to formulate a forensic conclusion regarding the possibility of common origin between glass fragments and broken glass objects, it is essential to examine the variations that can be expected for the object that broke. It is also important to assess the variation in these properties for a population of similar objects. Such within-source and between-source variations have been reported for many of the parameters (thickness, density, refractive index, composition) used in forensic glass comparisons. Variations in these properties have been studied for window glass, tempered glass, container glass and headlamp glass, which are the major glass types encountered in casework. Between-source variations are generally reported as frequency of occurrence histograms based on survey data. It must be recognized that the variation within an object is specific to that object and that only trends in expected variations can be established by examining the results from case studies. Any variations that are observed are also compared to the error associated with the technique in order to predict whether these variations can be anticipated in routine examinations.

Though the necessity of acquiring this information has long been recognized, only the more current studies will be addressed. Underhill (1980) was able to distinguish surface fragments (5-7 microns in thickness) from the bulk glass and reports that float surface fragments have a refractive index considerably higher than that of the bulk glass, typically 0.001 - 0.005 (corresponding match temperatures are lower).

The acquisition of surface RI data is difficult and time consuming. Generally the proportion of bulk glass far exceeds that of surface glass and it is conceivable that this effect may not be measurable in casework since orientation of the surface is also important. Variations in surface RI across a sheet of glass are reported to be 0.0009 while variations in RI across a sheet for the bulk glass is 0.0002.

Davies *et al.* (1980) confirm that the tin-contact surface in float glass has a refractive index typically 0.002 RI units higher than that of the bulk glass. There seems to be no correlation between the float RI and the bulk RI so that measurement of both these properties would increase the discriminating power of a comparison. Differences in RI of up to 0.0002 were noticed between the surfaces of patterned glass while no such variations in refractive index between surface and bulk glass was observed for non-float (sheet) window glass. Comparison of refractive index data for the bulk glass showed an average range of RI for tempered float windscreen glass was in the order of 0.0002 while that for float window glass was approximately 0.00003.

Studies on the variability of the refractive index throughout the thickness of the glass (Locke and Hayes 1984) showed that thick panes of glass were more variable in RI than thin panes, regardless of whether the pane had been tempered or not. The standard deviation in RI associated with thick, tempered glass was reported to be 0.00018 while thinner tempered sources had a standard deviation of about half that. Likewise, window glasses under 4 mm thick typically had associated standard deviations of 0.00007 or less while for much thicker samples (10 mm), a maximum standard deviation of 0.00013 was observed. By considering the variations across the pane and not just throughout its thickness, a standard deviation in RI of 0.00016 could be expected from a tempered source such as a windscreen. Local studies on tempered and non-tempered sources support these findings.

Surface variations in refractive index values are also observed on non-float windows and containers, some of the variations being quite large (Zoro *et al.* 1988).

Studies on between-sample variation usually result in a collection of frequency of occurrence data. Lambert and Evett (1984) have reported on refractive index data accumulated from control samples submitted in casework. Buckleton *et al.* (1986) reported on distributions of refractive index, thickness and color for glass originating from vehicles in New Zealand. Studies of this type constitute the data that is included today on computerized data bases. The design of one such data base for the UK using the Sapphire DATAEASE package is described by Winstanley *et al.* (1988).

The RCMP forensic laboratories have also created a prototype glass database from DBASE IV which was first described at the 1988 Canadian Society of Forensic Science Conference. This database is capable of assimilating data on refractive index before and after annealing, density, thickness, and chemical composition as well as other parameters that describe the glass and its source. The files are separated into CRIME (for control samples of glass submitted in casework), SURVEY (specific surveys) and EXHIBIT (glass fragments recovered from the clothing or footwear submitted in casework). Queries can be accomplished by the entry of specific data on a pre-formatted table or by means of a more versatile search argument. The results of a query can be presented in the form of a detailed report, a summary report containing frequently accessed information, or as chart displays such as frequency distributions. The data incorporates contributions from the seven laboratories across Canada and can be accessed nationally or regionally. Though this database is still in the development stages, it can be used to access data collections to aid in the interpretation of evidence for court and its versatility is only starting to be realized.

The ability to discriminate glass samples is dependent upon both the variation within the sample and the variations observed within an appropriate glass population. Large variations within a sample translate to a greater proportion of similar sources within any given data set.

II - Glass on Clothing and Footwear

Not only is it important to be able to assess the value of the analytical results by examining the variations observed and those expected, but it is equally important to render an opinion on how likely it is to find glass fragments on clothing and footwear. Unfortunately, there have been few papers written on the topic. In a paper by Pearson *et al.* (1971) men's jackets and trousers from a dry cleaners were searched for paint and glass. Results showed that 63 % of the suits bore glass (total of 551 fragments). Two suits contained 46 % of the glass found. The largest fragment was 7.1 mm in length, 18 fragments were longer than 1.0 mm and 128 fragments were longer than 0.5 mm. The majority of the recovered glass was colorless. The refractive index of the recovered glass was also determined, and the results plotted in histogram form. It must be noted that clothing worn by the general population might contain fewer glass fragments than that reported since clothing from a dry cleaning establishment can be expected to bear a larger amount of debris. Glass was recovered from pockets and cuffs where the retention times can be expected to exceed that of loose surface fragments. Note that the manner in which a suspect garment is searched may affect the probative value of the glass fragments found for these reasons.

The examination of footwear for the presence of glass fragments poses a special problem since it is generally expected that footwear is commonly exposed to sources of broken glass on the ground. In a survey of 650 pairs of men's shoes collected from donations to Goodwill, 261 out of 1300 shoes (≈20%) bore embedded or trapped colorless glass (Davis and DeHaan 1977). Eighty-two (82) % of these shoes bore less than four fragments. Colored glass fragments were recovered from only 6% of the shoes and 42% of the shoes bore no detectable trace evidence. Glass fragments were more frequently found in rubber soles than other types and the crepe soles, surprisingly, retained little trace evidence at all. Fluorescence was detected in about 12% of the colorless glass fragments found and over 70% of the glass fragments were 0.17-0.84 mm long. Only 5% of the glass fragments were over 2 mm long. Refractive index determinations were made on 366 of the larger fragments. Loose contact glass was not reported because of the probability of cross contamination. It was not possible to comment on the probability of contact with a heavily contaminated source as opposed to random accumulation by merely examining the number of fragments embedded in the soles.

Walsh and Buckleton (1986) directly address the problem of comparing the refractive index of colorless glass fragments embedded in footwear to a data base collection of RI values for glass collected from scenes of crime generally that contains mainly glass from buildings. A bias is unfairly introduced since refractive index distributions for containers and flat glass sources are different. It is assumed in this study that glass embedded in footwear results from an individual standing on glass. In an attempt to simulate the population of glass available to be embedded in footwear during normal activity, 52 km of pathways in four different urban environments were searched for colorless glass fragments larger than 0.3 mm. Classification of the 1068 samples collected into types (container, headlamp lens, headlamp reflector, vehicle window, building window mirror or bulb) was accomplished by examining the gross physical attributes of the large fragments. Container glass accounted for 70% of all the glass collected (no effect from urban areas), 12% was attributed to building window glass, 9% to vehicle window glass (tempered) and 5% to headlamp glass. A population of this nature would be more indicative of that on footwear resulting from non-crime related exposure to glass embedded in footwear.

The retention of glass fragments on a blended wool-acrylic fabric and on denim was studied by firing 100 mg of glass fragments of a single size (125 µm to 4 mm in sample sizes were tested) onto 30 x 30 cm swatches of both fabrics (Brewster *et al.* 1985). The swatches were fastened to laboratory coats worn by subjects pursuing normal activities and were removed after pre-determination time intervals. A number of trends were observed in particle retention. All particle sizes were rapidly lost from both fabrics. It was possible to find a small number of particles (<3) on the fabrics even after five days. The number of particles transferred initially to the wool exceeded that transferred to the denim, the result thought to be a function of the looser weave of the wool. The authors caution that the transfer mechanism used in this study may not simulate that of backward fragmentation.

A report on innocent exposure to broken glass, resulting from a written survey to the general population, was prepared by Zoro and Fereday (1986). The survey recorded that for a seven day period, 1 person in 3 is exposed to breaking glass, 1 in 10 being exposed to more than one broken source. One male in 9 is exposed to a source of broken flat glass (building and car windows). Females are exposed to broken household objects more frequently than males and lighting fixtures account for 5% of all breakages. This type of information will aid the forensic scientist in assessing the significance of finding glass in casework.

Harrison *et al.* (1982) comment on the assimilation of data from casework on glass fragments that match a control sample vs the non-match fragments. The study involved the distribution of refractive indices for over 2000 glass fragments recovered from clothing (195 cases). Though refractive index was the major criterion discussed for differentiation, other techniques that were involved in the comparisons were also considered. The highest proportion of glass that matched a control sample was recovered from the hair, loose glass from the surface of clothing was next, followed by loose fragments on footwear, then pockets and finally glass embedded in footwear. As such, the examination of footwear for glass fragments may not have much probative value. Likewise, data from glass from pockets should be scrutinized because of its retentability. The data was grouped statistically in order to relate to glass sources instead of individual fragments.

For the non-matching fragments, the refractive index distribution for the glass recovered from the surface of the clothing is different than that for the glass embedded in footwear (which shows a similarity to the RI distribution for container glass). The majority of non-matching glass in the survey from both clothing and footwear was of non-window origin. While the RI distribution of matching glass fragments echoes that of the control samples, the RI distribution of the non-matching fragments is markedly different. Comparison of results to a control glass data base may be misleading unless there is some mechanism to establish glass type or origin. If this is possible, the control glass data can be accessed according to the type of glass predicted. This report states unequivocally that, "The collection of control glass data is not a reliable guide to the probability of finding glass of a particular RI on the clothing of an individual". The interpretation of glass evidence is a very complicated task and as such, has been the study of many statistical interpretations that could aid the forensic glass examiner in their task of assigning a forensic significance to their analytical results.

III - Statistics

In practice, the approach taken for assessing the strength of all physical evidence generally follows the argument presented here for glass. If suspect glass is found to match control glass, that glass could have originated from the broken source in question, or from another source of broken glass having the same measured properties. The question then becomes, "How many other broken sources exist in the random glass population that would be similar to the control glass (and thus the suspect glass) in those measured properties?" A smaller number of alternate sources is indicative of stronger forensic evidence. This is the philosophy of the coincidence theory and attempts to address the likelihood that the suspect glass is present by coincidence.

Evett (1986) and Grove (personal communication) have both independently addressed the statistical interpretation of refractive index in very complicated, mathematical terms.

The probative value of forensic glass evidence has been broached using a Bayesian approach that describes the use of likelihood ratios based on two scenarios (Evett 1986).

Firstly, the glass recovered from the suspect's clothing or footwear resulted from the suspect breaking the glass object at the crime scene (association). Secondly, the recovered glass was innocent and someone else broke the glass object at the crime scene (non-association). The presentation is discussed for refractive index measurements only, but the theory could be extended to include information from other analytical techniques. The theory requires information on the number of people in the general population who have glass on their clothing and the RI distributions of such a population. Information on the transfer, persistence and recovery of glass fragments is also necessary, as well as frequency histograms of the measured property (such as RI) for a particular type of control sample (container, flat). The data population that is used to assess the evidential value should be prudently selected. Examination of the likelihood ratio for one or two fragments conceptually corroborates an examiners' intuitive assessment of glass evidence. Though the mathematical treatment for a large number of fragments is complicated, the amount of glass found has been recognized to be relevant to the assessment of evidential value. After establishing values for the likelihood ratios for two glass fragments in numerical terms, Evett (1986) renders the opinion that the evidential value of a match is generally underestimated.

Evett and Buckleton (1988) pursue the Bayesian approach to the interpretation of glass evidence and include arguments based on groupings of glass from a suspect and comparisons of the group to the control rather than assessing individual fragments. They refer to a Belfast clothing survey based on the quantity of glass found on garments from people with no known connection to crime. The result of this survey indicate that only 2.9% of these people have three or more fragments of glass on their clothing, so that a group of three or more fragments could be considered large. Again, this paper emphasizes the need for more survey and experimental data of the type required to support these statistical hypotheses.

Though Bayes theorem was useful for combining data on the occurrence of glass on clothing, RI distributions and the transfer of glass (backward fragmentation), the Bayesian approach, even in simplified form, became complex when trying to interpret the evidential value of multiple groups recovered from a suspect source and multiple control glass sources. In order for the forensic scientist to cope with this, an interactive computer program has been developed to assist in the interpretation of glass evidence (Buckleton *et al.* 1989). This system provides information from data bases, allows subjective judgements by the users and even stores the results of previous judgements. In this way the system is perceived as one that provides data, advice and computational power. Using this information, the examiner retains the responsibility of making the final judgements given the circumstances of the case.

CONCLUSION

Glass as trace evidence is a complex topic that has received much study. Recent developments in technology have not only affected the analytical approach to forensic glass comparisons, but also the conceptual approach to the interpretation of that data in assessing its evidential value. This review was intended to highlight some of these developments in the context of existing methodologies and provoke questions that may stimulate additional research.

REFERENCES

Andrasko, J. and Maehly, A. C. (1978). The discrimination between samples of window glass by combining physical and chemical techniques, J. Foren. Sci 23:250-262.

Beveridge, A. D. and Semen, C. (1979). Glass density measurement using a calculating digital density meter, Can. Soc. Foren. Sci. J. 12:113-116.

Brewster, F., Thorpe, J. W., Gettinby, G. and Caddy, B. (1985). The retention of glass particles on woven fabrics, J. Foren. Sci. 30:798-805.

Buckleton, J. S., Axon, B. W. and Walsh, K. A. J. (1986). A survey of refractive index, color and thickness of window glass from vehicles in New Zealand, Foren. Sci. Int. 32:161-170.

Buckleton, J., Pinchin, R. and Evett, I. (1989). Computerized assistance for glass evidence (CAGE): Experimental knowledge based system for assisting in the interpretation of forensic glass examinations, CRSE Report No. 689.

Dabbs, M. D. G. and Pearson, E. F. (1970). The variation in refractive index and density across two sheets of window glass, J. Foren. Sci. Soc. 10:139-148.

Dabbs, M. D. G. and Pearson, E. F. (1972). Some physical properties of a large number of window glass specimens, J. Foren. Sci. 17:70-78.

Davies, M. M., Dudley, R. J. and Smalldon, K. W. (1980). An investigation of bulk and surface refractive indices for flat window glasses and windscreen glasses, Foren. Sci. Int. 16:125-137.

Davis, R. J. and. DeHaan, J. D. (1977). A survey of men's footwear, J. Foren. Sci. Soc. 17:271-285.

Dudley, R. J., Howden, C. R., Taylor, T. J. and Smalldon, K. W. (1980). The discrimination and classification of small fragments of window and non-window glasses using energy-dispersive x-ray fluorescence spectrometry, X-Ray Spectr. 9:119-122.

Evett, I. W. (1986). A bayesian approach to the problem of interpreting glass evidence in forensic science casework, J. Foren. Sci. Soc. 26:3-18.

Evett, I. W. and Buckleton, J. (1989). The interpretation of glass evidence: a practical approach, CRSE Report No. 680.

Fong, W. (1973). The value of glass as evidence, J. Foren. Sci. 18:398.

Greene, R. S. and Burd, D. Q. (1965). Individualization of glass specimens, J. Foren. Sci. 10:52-59.

Harrison, P. H., Lambert, J. A. and Zoro, J. A. (1982). A survey of glass fragments recovered from clothing of persons suspected of involvement in crime, HOCRE Report No. 458.

Hickman, D. A., Harbottle, G. and Sayre, E. V. (1983). The selection of the best elemental variables for the classification of glass samples, Foren. Sci. Int. 23:189-212.

Hickman, D. A. (1983). Elemental analysis and the discrimination of sheet glass samples, Foren. Sci. Int. 23:213-223.

Howden, C. R., Dudley, R. J. and Smalldon, K. W. (1978).

The analysis of small glass fragments using energy dispersive x-ray fluorescence spectrometry, J. Foren. Sci. Soc. 18:99-112.

Keeley, R. H. and Christofides, S. (1979). Classification of small glass fragments by x-ray microanalysis with the SEM and a small XRF spectrometer, Scanning Electron Microsc. 1:459-464.

Koons, R. D., Fiedler, B. A. and Rawalt, R. C. (1988). Classification and discrimination of sheet and container glasses by inductively coupled plasma-atomic emission spectrometry and pattern recognition, J. Foren. Sci. 33:49-67.

Lambert, J. A. and Evett, I. W. (1984). The refractive index distribution of control glass samples examined by the forensic science laboratories in the United Kingdom, Foren. Sci. Int. 26:1-23.

Lloyd, J. B. F. (1981). Fluorescence spectrometry in the identification and discrimination of float and other surfaces on window glasses, J. Foren. Sci. 26:325-342.

Locke, J. (1985). GRIM — a semi-automatic device for measuring the refractive index of glass particles, The Microscope 33:169-178.

Locke, J., Badmus, H. O. and Perryman, A. C. (1985). A study of the particles generated when toughened windscreens disintegrate, CRE Report No. 581.

Locke, J. and Elliott, B. R. (1984). The examination of glass particles using the interference objective. Part 2: A survey of flat and curved surfaces, Foren. Sci. Int. 26: 53-66.

Locke, J. and Hayes, C. A. (1984). Refractive index variations across glass objects and the influence of annealing, Foren. Sci. Int. 26:147-157.

Locke, J. and Perryman, A. C. (1985). The evidential value of dispersion in the examination of glass, CRE Report No. 589.

Locke, J. and Rockett, L. A. (1985). The application of annealing to improve the discrimination between glasses, Foren. Sci. Int. 29:237-245.

Locke, J., Sanger, D. G. and Roopnarine, G. (1982). The identification of toughened glass by annealing, Foren. Sci. Int. 20:295-301.

Locke, J. and Underhill, M. (1985). Automatic refractive index measurement of glass particles, Foren. Sci. Int. 27:247-260.

Locke, J. and Unikowski, J. A. (1989a). Breaking of flat glass part 1: size and distribution of particles from plain glass windows, CRSE Report No. 663.

Locke, J. and Unikowski, J. A. (1989b). Breaking of flat glass part 2: effect of pane parameters and particle distribution, CRSE Report No. 702.

Locke, J., Winstanley, R., Rockett, L. A. and Rydeard, C. (1985). A comparison of long and short schedules for the annealing of glass particles, Foren. Sci. Int. 29:247-258.

Luce, R. J. W., Buckle, J. L. and McInnis, I. (1991). A study on the backward fragmentation of window glass and the transfer of glass fragments to individual's clothing, Can. Soc. Foren. Sci. J. 24:

Marcouiller, J. M. (1990). A revised glass annealing method to distinguish glass types, J. Foren. Sci. 35:554-559.

McCrone, W. C. (1974). Microscopical characterization of glass fragments, J. Assoc. Off. Anal. Chem. 57:668-670.

Miller, E. T. (1976). Glass density method using mettler balance, Crime Lab. Digest 76 (4):6

Nelson, D. F. and Revell, B. C. (1967). Backward fragmentation from breaking glass, J. Foren. Sci. Soc. 7:58-61.

Ojena, S. M. and DeForest, P. R. (1972). Precise refractive index determination by the immersion method, using phase contrast microscopy and the mettler hot stage, J. Foren. Sci. Soc. 12:315-329.

Pearson, E. F., May, R. W. and Dabbs, M. D. G. (1971). Glass and paint fragments found in men's outer clothing - report of a survey, J. Foren. Sci. 16:283-300.

Pitts, S. J. and Kratochvil, B. (1991). Statistical discrimination of flat glass fragments by instrumental neutron activation analysis methods for forensic science applications, J. Foren. Sci. 36:122-137.

Pounds, C.A. and Smalldon, K. W. (1978). The distribution of glass fragments in front of a broken window and the transfer of fragments to individuals standing nearby, J. Foren. Sci. Soc. 18:197-203.

Reeve, V., Mathiesen, J. and Fong, W. (1976). Elemental analysis by energy dispersive x-ray: a significant factor in the forensic analysis of glass, J. Foren. Sci. 21:291-306.

Ryland, S. G. (1986). Sheet or container? - forensic glass comparisons with an emphasis on source classification, J. Foren. Sci. 31:1314-1329.

Saferstein, R., ed. (1982). Forensic Science Handbook, Prentice-Hall Inc., Englewood Cliffs, NJ.

Sanger, D. G. (1973). The identification of toughened glass using polarized light, J. Foren. Sci. Soc. 13:29-32.

Slater, D. P. and Fong, W. (1982). Density, refractive index, and dispersion in the examination of glass: their relative worth as proof, J. Foren. Sci. 27:474-483.

Stoney, D. A. and Thornton, J. I. (1985). The forensic significance of the correlation of density and refractive index in glass evidence, Foren. Sci. Int. 29:147-157.

Terry, K. W., Van Reissen, A., Lynch, B. F. and Vowles, D. J. (1984). Quantitative analysis of glasses used in Australia, Foren. Sci. Int. 25:19-34.

Uhlmann, D. R. and Kreidl, N. J. (eds.). (1984). Glass Science and Technology, Vol. 2, Academic Press Inc., NY.

Underhill, M. (1980). Multiple refractive index in float glass, J. Foren. Sci. Soc. 20:169-176.

Walsh, K. A. J. and Buckleton, J. S. (1986). On the problem of assessing the evidential value of glass fragments embedded in footwear, J. Foren. Sci. Soc. 26:55-60.

Winstanley, R. and Rydeard, C. (1985). Concepts of annealing applied to small glass fragments, Foren. Sci. Int. 29:1-10.

Winstanley, R., Newall, R. and Ford, A. (1988). A new data base for glass, CRSE Technical Note No. 657.

Zoro, J. A. (1983). Observations on the backward fragmentation of float glass, Foren. Sci. Int. 22:213-219.

Zoro, J. A. and Fereday, M. J. (1986). Report of a survey concerning the exposure of individuals to breaking glass, CRE Report No. 592.

Zoro, J. A., Locke, J., Day, R. S., Badmus, O. and Perryman, A. C. (1988). An investigation of refractive index anomolies at the surfaces of glass objects and windows, Foren. Sci. Int. 39:127-141.

IDENTIFICATION OF WOOD FRAGMENTS IN TRACE EVIDENCE

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From time to time, wood plays an important role in solving criminal cases. Wood samples vary in size and can range from trees and logs to pieces as small as individual wood fibers. Botanists can easily identify trees, especially when the leaves, flowers, or fruits are present. Using standard techniques, wood technologists, foresters, and wood anatomists can generally identify logs, lumber, wood products, and pieces of wood bigger than a matchbox. As the size of the piece decreases, however, accurate determinations are more difficult. Very small fragments require special handling and identification techniques. This paper describes the techniques used at the USDA Forest Service, Forest Products Laboratory (FPL) to handle and identify different sizes of wood fragments. Some examples of actual cases are also presented.

TECHNIQUES AND EQUIPMENT

Wood anatomy and identification is studied at the macro- and microscopic level. At the macroscopic level, the naked eye and a hand lens (10X to 20X) are routinely used. The wood is examined on the cross (transverse), radial, and tangential sections where various features can be seen (Figure 1). The cross section (X) is that surface or section that is cut perpendicular to the grain—the surface that can be seen when looking at the end of a log or the top of a stump. The radial section (R) is that surface or section cut along the grain in a radial plane—the surface exposed if a piece of wood is split down the middle from the pith (center of the tree) to the bark. The tangential section (T) is that surface or section cut along the grain in a tangential plane—the surface exposed when the bark is removed from a tree or the plane tangent to the growth rings. Each of these sections exhibits different aspects of the wood, and it is critical in identification to cut and view the wood in true cross, radial, and tangential sections. For macroscopic identification, the cross section is the most important area. Foresters and wood technologists often examine and identify lumber and wood products of north temperate species using only the naked eye and hand lens. Books on macroscopic wood anatomy and identification are generally targeted for the forest science audience and include works by Hoadley (1980, 1990), Core *et al.* (1979), Edlin (1977), Panshin and deZeeuw (1980), and White (1980).

At the microscopic level, scientists most often use the light microscope with low (4X to 10X) to high (25X to 100X) power objectives, but the scanning electron microscope (SEM) has gained favor in recent years (Core *et al.* 1979). Again, it is important that the wood is cut and viewed in true cross, radial, and tangential sections. Generally, microscopic wood anatomy is coupled with macroscopic anatomy, and the targeted audiences are plant and wood anatomists. Books on macro- and microscopic wood anatomy include Metcalfe and Chalk's (1950) two-volume descriptive work on all the major plant families; recent revisions of the Anatomy of the Dicotyledons by Metcalfe and Chalk (1979, 1983) and Metcalfe (1987); Carlquist's (1988) book on comparative wood anatomy; the Raven *et al.* (1986) textbook on biology; and publications by Miller (1981) and the IAWA Committee (1989) on diagnostic features for hardwood identification. Additional important books and papers slanted toward wood identification include works by Brazier and Franklin (1961), Core *et al.* (1979), Grosser

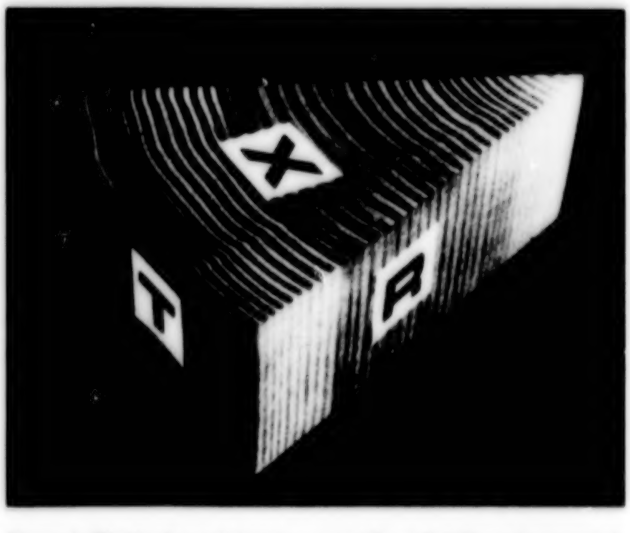


Figure 1. Block of wood showing cross (X), radial (R), and tangential (T) sections.

(1977), Kribs (1968), Kukachka (1960), Panshin and deZeeuw (1980), Phillips (1979), and Schweingruber (1990).

The technique I use at FPL for identifying wood involves two major steps. The first is the macroscopic examination of the unknown wood sample with naked eye and a hand lens. The second is a microscopic examination of thin sections of the radial and tangential sections.

The naked eye examination is used mainly to visually determine the color, odor, weight, and unusual features or defects of the wood. However, it might also include a chemical test such as the froth and fluorescent tests (Miller 1981; IAWA Committee 1989), spot-test for aluminum (Kukachka and Miller 1980), and sodium nitrite spot-test (Miller *et al.* 1985). The naked-eye examination and the chemical tests often reveal some clues to the identity of the wood. Next, the surface of the cross section is smoothed with a sharp knife (microtome or utility knife) or razor blade. The utility or microtome knife is best for large samples, but for samples the size of matchsticks, the razor blade works better. The smoothed cross-section is then examined with a hand lens. Wetting the surface enhances the contrast and generally reveals more detail. I use a 14X triplet, which gives good resolution and a wide field of view. Based on the combination of a few diagnostic features, experienced wood anatomists can often make a tentative identification if the sample is larger than a matchbox and it is a hardwood.

To examine the wood with a light microscope, thin radial and tangential sections are cut from the sample. Standard microtechniques can be used to cut, stain, and mount the sections. However, to save time, I cut thin sections with a hand-held microtome knife (Figure 2). Again, a utility knife with replaceable blades or a single-edge razor blade also works well. It is critical that the wood sample is oriented properly so that true radial and tangential sections are cut. The actual cutting procedure is difficult to describe, but it is much like peeling an apple with a pocketknife (Figure 2). The peeled sections need not be as large, as evenly thin, or as perfect as microtomed sections. Practice is the key to cutting quality sections. As the sections are cut, they are transferred from the blade directly to the slide. Staining is not required. Next, a few drops of a 50-50 solution of ethanol and glycerine are added as a mounting media. The coverslip is then put in place and the slide is transferred to a hotplate where the slide is heated to boil the ethanol. Boiling replaces the air in the cells with glycerine and essentially clears the sections for viewing. Water can also be used as a mounting medium, but the temperature of the hotplate must be raised and often the water boiling action is erratic and severe. To increase contrast or to detect some particular features, especially silica, combinations of glycerine, ethanol, and water are useful. Sometimes removing the coverslip from a boiled glycerine/ethanol mount and adding a drop or two of water is sufficient.

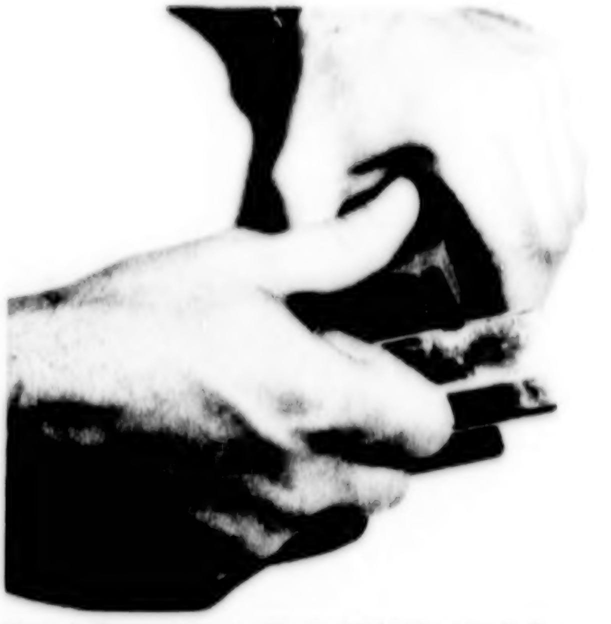


Figure 2. Thin sections cut with a hand-held microtome knife.

For small samples, the razor blade is used to cut the sections. If razor blades are to be used to cut large samples, I recommend splitting a small piece from the larger one. If the sample is too small to hold between the fingers, use tweezers to hold it. If the sample is too small for tweezers, try taping it to an index card and then cutting through the tape and wood. If that does not work, try holding the sample on a slide and slicing through it in any direction that works. The section most likely will not be oriented correctly, but some features may still be visible that can help with an identification. If the sample is so small that it cannot be sectioned, put the entire sample on the slide and treat it as a thin section. The sample might be too thick in some areas, but areas at the edges can often be viewed. Another method for handling small specimens is to use a reflective light microscope or the SEM. Both microscopes allow the operator to view the surface of the specimen. All the anatomical features are present, but most features appear quite different. However, depending on the sample, a smooth surface might still be necessary.

After the unknown wood is examined with the naked eye, hand lens, and light microscope, several methods can be used to identify the wood. Dichotomous wood anatomical keys (Core *et al.* 1979; Kribs 1968), tables of data (Kukachka 1960; Phillips 1979), marginally edge-punched cards (Brazier and Franklin 1961), anatomical descriptions (Panshin and deZeeuw 1980), photomicrographs (Miles 1978), and computer-assisted programs and databases (Wheeler *et al.* 1986; Ilic 1987, 1990; Miller 1981) are useful tools and literature sources to assist in the identification process. Of course, expert recognition is the best method, but this requires identification of the sample simply through examination of the wood. Although this is the best method of identification, it takes years of practice and can only be employed by an expert. However, even an expert needs to follow the methods previously mentioned when the wood is not recognized or he or she has doubts about the identification. In any case, when a tentative identification is made, it is important to compare the unknown sample with authentic wood samples and slides in a reference collection. If such a collection is not available, start one by buying wood identification kits and/or samples, accumulating samples that have already been identified, and trading samples with others (see Hoadley 1990 for names and addresses). At the very least, compare your findings with the literature sources previously mentioned.

WOOD ANATOMY

Wood is a complex fibrous substance made up of specialized cells. The size, shape, type, and pattern in which these cells are laid down to form wood varies from family to family, genus to genus, species to species, and even within a species. The task of the wood anatomist is to determine the extent of variation and to interpret whether the differences are the effects of environmental conditions or habitat, or whether they reflect genetic differences.

Woods are divided into two major categories: hardwoods and softwoods. Hardwood trees (angiosperms) generally have broad leaves, are generally deciduous in temperate regions, and contain specialized cells called vessel elements (Figure 3). Softwood trees (conifers or gymnosperms) are cone bearing, generally have scalelike or needlelike leaves, are not deciduous, and do not contain vessel elements (Figure 3). The terms hardwood and softwood have no direct application to the hardness or softness of the wood. In fact, hardwood trees such as cottonwood, aspen (several species of *Populus*), and balsa (*Ochroma pyramidale*) have softer wood than the yellow pines (several species of Pinus) and Douglas-fir (*Pseudotsuga menziesii*), which are softwoods.

Wood is essentially all the material under the bark. The cambium, a thin layer of cells between the bark and wood, is the active growing area where the cells divide and eventually differentiate to form bark cells to the outside and wood cells to the inside (Figure 4). This

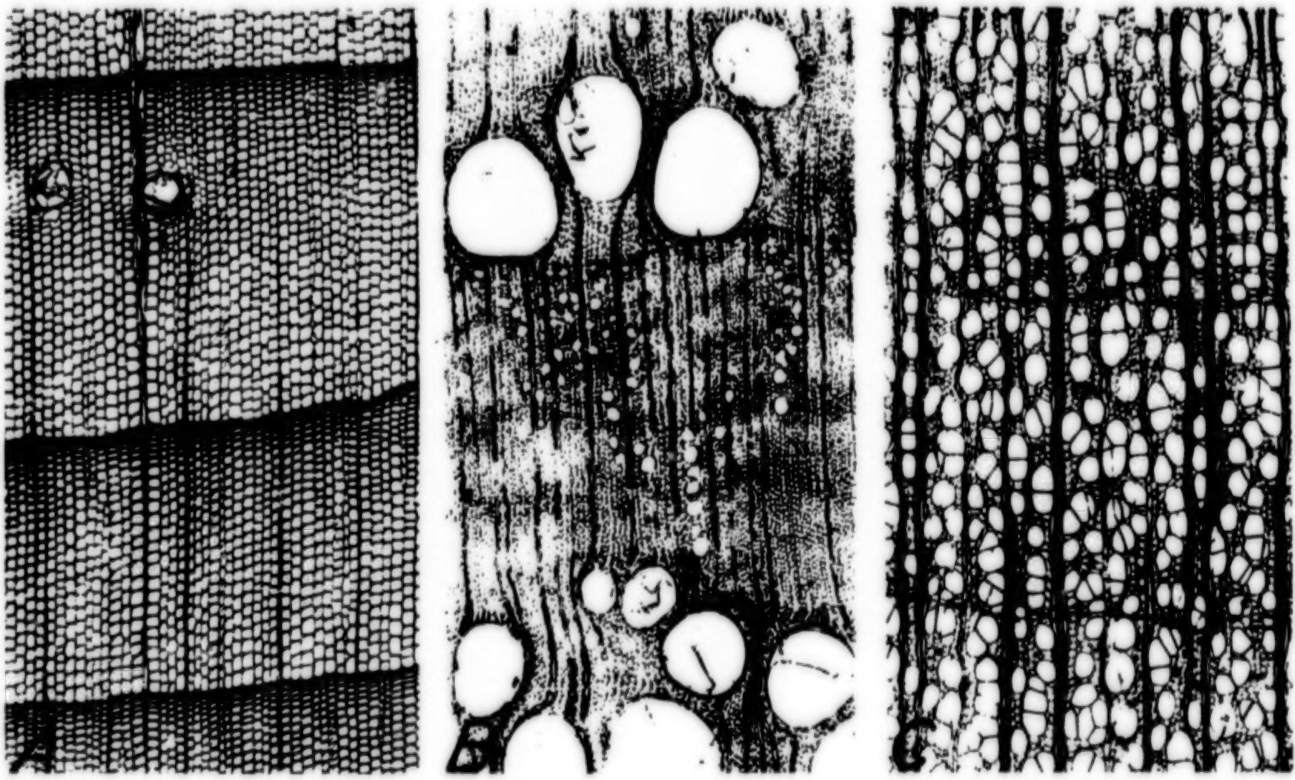


Figure 3. Cross sections of softwood and hardwood. A, softwood — vessels are absent; large openings toward top are resin ducts. B; hardwood — two distinct sizes of vessels arranged in distinct pattern or ring (ring-porous). C, hardwood — essentially one size of vessel arranged in diffuse pattern (diffuse-porous).

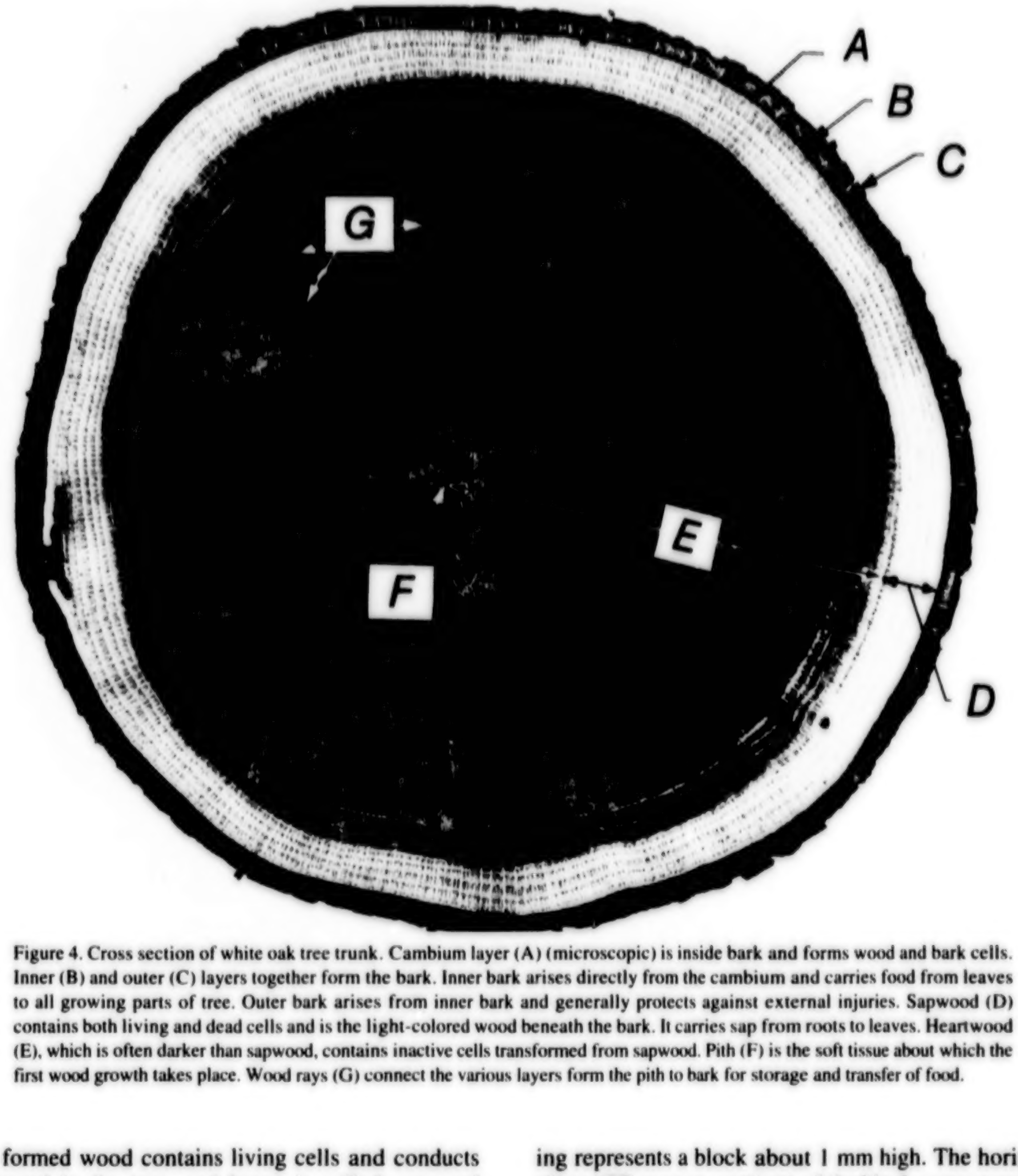


Figure 4. Cross section of white oak tree trunk. Cambium layer (A) (microscopic) is inside bark and forms wood and bark cells. Inner (B) and outer (C) layers together form the bark. Inner bark arises directly from the cambium and carries food from leaves to all growing parts of tree. Outer bark arises from inner bark and generally protects against external injuries. Sapwood (D) contains both living and dead cells and is the light-colored wood beneath the bark. It carries sap from roots to leaves. Heartwood (E), which is often darker than sapwood, contains inactive cells transformed from sapwood. Pith (F) is the soft tissue about which the first wood growth takes place. Wood rays (G) connect the various layers form the pith to bark for storage and transfer of food.

newly formed wood contains living cells and conducts sap upward in the tree, and hence is called sapwood (Figure 4). Eventually the inner sapwood cells become inactive and are transformed into heartwood (Figure 4). This transformation is often accompanied by the formation of extractives that darken the wood and give species such as walnut (*Juglans nigra*), a Brazilian rosewood (*Dalbergia nigra*), and redwood (*Sequoia sempervirens*) a characteristic color.

Structure of Typical Hardwood

Figure 5 illustrates the cellular structure of yellow-poplar (*Liriodendron tulipefera*) as an example of a hardwood (Forest Products Laboratory 1980). The drawing represents a block about 1 mm high. The horizontal plane (TT or cross section) of the block corresponds to a minute portion of the top surface of a stump or end surface of a log. The vertical plane (RR or radial section) corresponds to a surface cut parallel to the radius and parallel to the wood rays (WR). In Figure 4, the wood rays radiate from the pith (center portion of the tree) like spokes of a wheel. The vertical plane (TG or tangential section) corresponds to a surface cut at right angles to the radius and the wood rays, or tangentially within the log. The appearance of these three major planes (Figures 2,5)—cross, radial, and tangential—is very different and the orientation of the planes is critical in any observations.

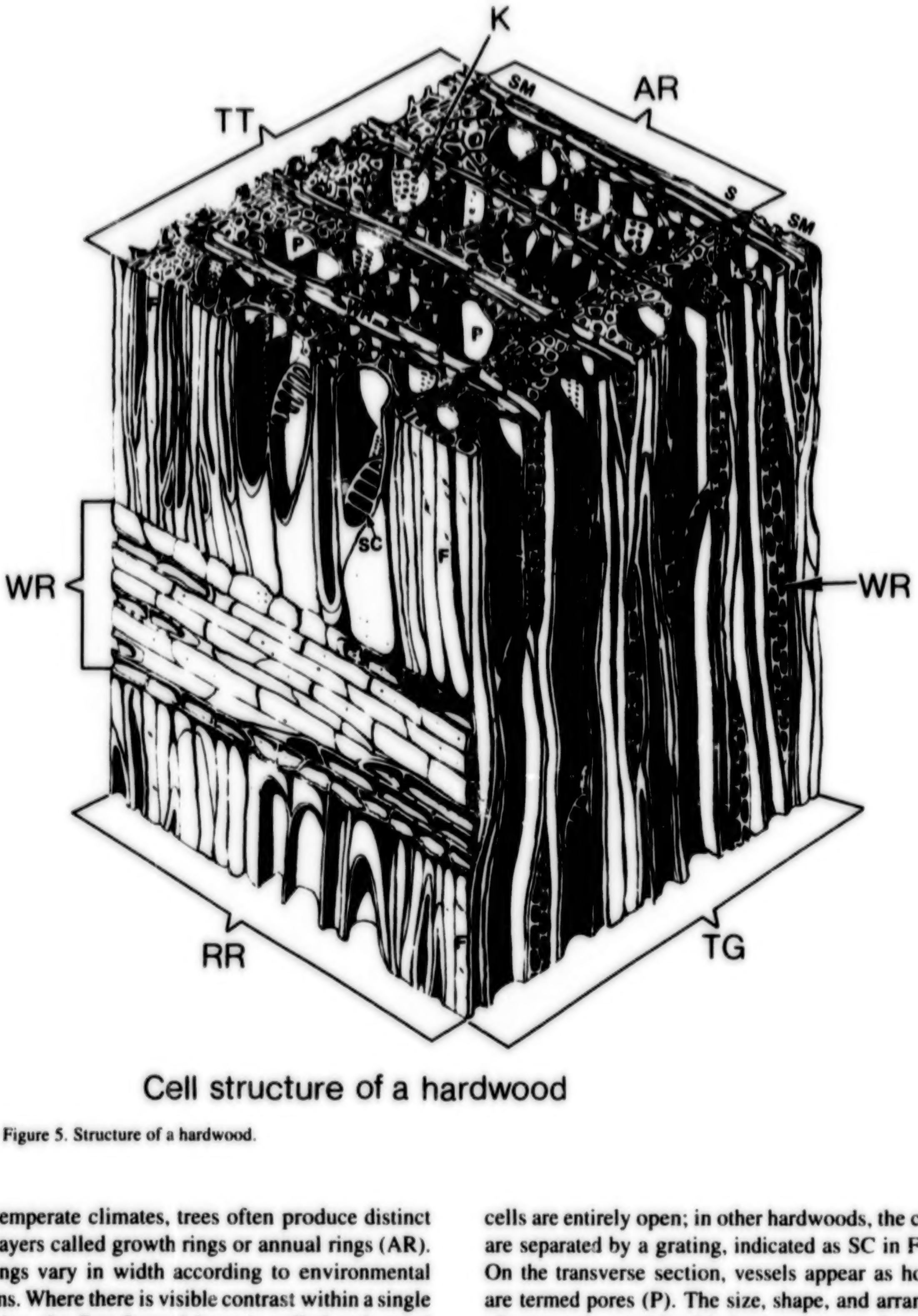


Figure 5. Structure of a hardwood.

In temperate climates, trees often produce distinct growth layers called growth rings or annual rings (AR). These rings vary in width according to environmental conditions. Where there is visible contrast within a single growth ring, the first formed layer is called earlywood (S) and the remainder latewood (SM).

Hardwoods have specialized structures called vessels for conducting sap upward. Vessels are a series of relatively large cells with open ends set one on top the other and continuing as open passages for long distances. In most hardwoods, the ends of the individual cells are entirely open; in other hardwoods, the cell ends are separated by a grating, indicated as SC in Figure 5. On the transverse section, vessels appear as holes and are termed pores (P). The size, shape, and arrangement of pores vary considerably between species but are relatively constant within a species. Most of the smaller cells on the transverse section are wood fibers (F), which function as support and give strength to the wood. Thin places or pits (K) in the walls of the fibers and vessels allow sap to pass from one cell to another. Wood rays (WR) are strips of short horizontal cells that extend in a radial direction. Their function is food storage and lateral conduction. In Figure 5, most of the rays in tangential section (TG) are two cells wide, but in different species of hardwoods, rays vary from 1 to more than 50 cells wide and from less than 100 μm to more than 100 mm in height.

Structure of Typical Softwood

Figure 6 illustrates the cellular structure of white pine (*Pinus strobus*) as an example of a softwood (Forest Products Laboratory 1980). Like the example of the hardwood in Figure 5, the drawing represents a wood block about 1 mm high. The three planes, transverse (TT), radial (RR), and tangential (TG), represent the same three planes described for hardwoods. The rectangular units that make up the transverse section (TT) are cuts through long vertical cells called tracheids or fibers (TR). Because softwoods do not contain vessels, the tracheids serve the dual function of transport and support. The wood rays (WR) function similarly to hardwood rays but are usually much smaller. Fusiform wood rays (FWR) are rays with horizontal resin ducts (HRD)

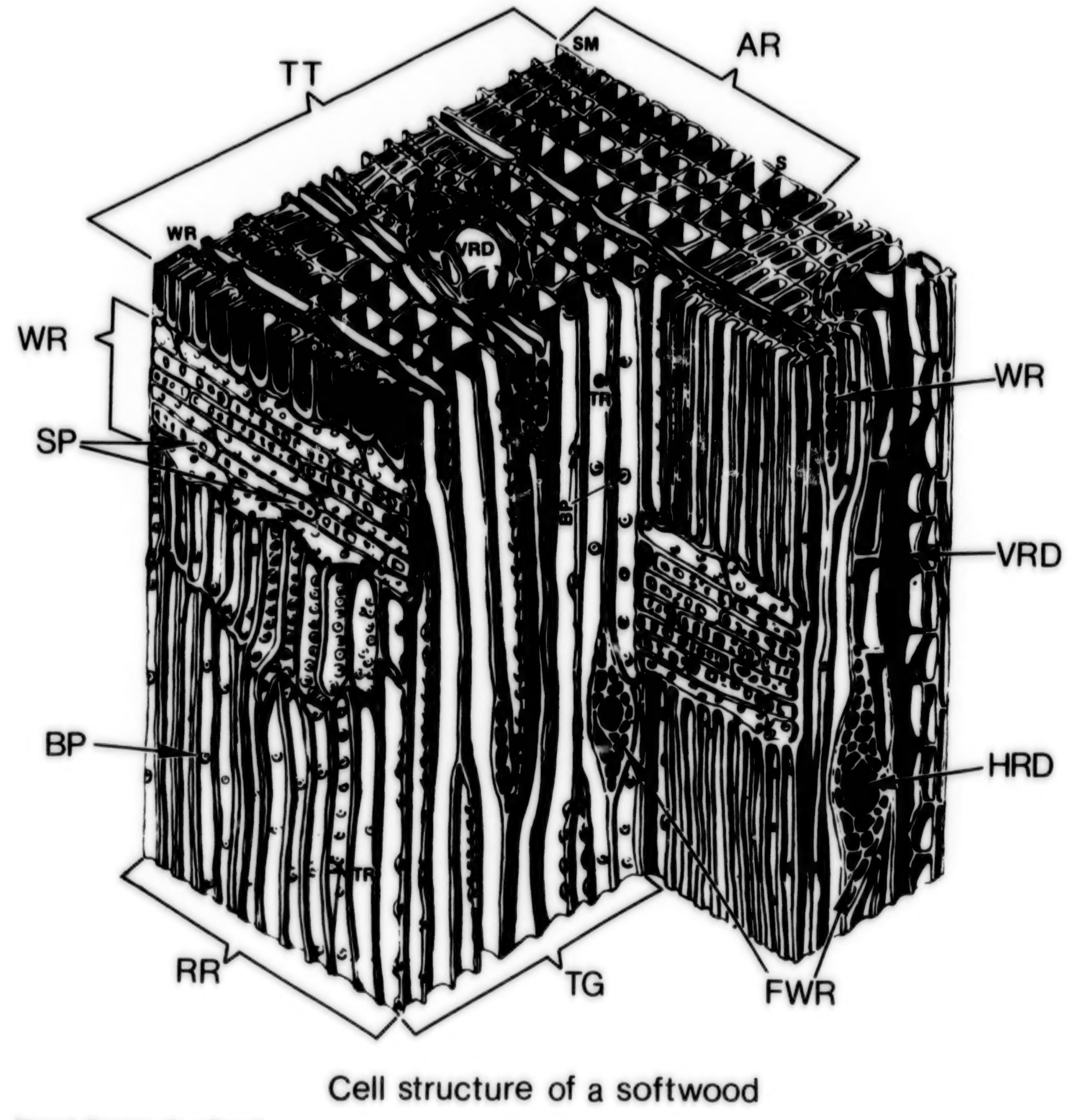


Figure 6. Structure of a softwood.

at their centers. The large hole in the center of the transverse section is a vertical resin duct (VRD). Some softwoods such as eastern red cedar (*Juniperus virginiana*) and true firs (*Abies* spp.) do not have resin ducts. The annual ring (AR) is often divided into an earlywood zone (S) composed of thin-walled cells and a latewood zone (SM) composed of thicker walled cells. The symbol SP indicates a simple pit, an unthickened portion of the cell wall through which sap passes from ray cells to tracheids or vice versa. The margins of bordered pits (BP) are overhung by the surrounding cell walls, but the pits still function as a passageway for sap to move from one cell to another. Under the light microscope, simple pits look like holes or openings and bordered pits look like doughnuts.

These few paragraphs on the basic structure of hardwood and softwoods are a brief introduction to the broad field of wood anatomy that includes disciplines such as ecology, systematics, phylogeny, and physiology. In this paper, wood anatomy is described as it relates to trace evidence. In this respect, two areas of wood anatomy are explored: comparative wood anatomy, where the macroscopic and/or microscopic wood anatomy of one piece is compared to another, and wood identification, where the macroscopic and/or microscopic anatomy is used to assign a botanical name to the piece.

Comparative Wood Anatomy

In forensic science, comparative wood anatomy generally refers to the matching of growth patterns in different pieces or to the examination of a piece for clues. In cases involving small fragments of wood, it is important to examine the possibility that a physical match may exist; that is, the small wood piece might have come from a larger one. The size, shape, color, and finish of the piece might be critical. A physical match is very strong evidence and should never be overlooked. In larger samples, tool marks on the wood may prove to be very important. The most famous of all cases in which wood anatomy was used to help solve a crime was the Lindbergh kidnapping case. Coincidently, it was also the first case where wood anatomy was used in the court system.

When the Lindbergh baby was kidnapped in the early morning hours of March 2, 1932, Arthur Koehler was an employee at the FPL. Several weeks after the crime, Koehler was asked to identify some splinters taken from the ladder that was left at the scene (Figure 7). In his response to the FBI, Koehler explained that he might be able to glean additional information from the ladder if he could examine the entire ladder. After 10 months of waiting, Koehler got the ladder and his chance to make history.

Koehler examined all 19 ladder parts in detail (Figure 7). He discovered marks left by hand saw, hand plane, chisel, and machine planer. He also noted square holes in one rail that did not correspond to the construction of the ladder. With this basic information, Koehler set out to find the mill that manufactured the boards with unique machine planer marks. After 6 months of searching, he found a match. He first went to the Dorn Mill in McCormick, South Carolina, and from there to the National Lumber and Millwork company in the Bronx, NY. Initially, this proved to be a dead end search because the lumber company operated on a cash basis and could not provide a list of customers. The date was November 1933.

In September 1934, Bruno Richard Hauptmann was arrested as a suspect in the Lindbergh case after he bought gasoline with the marked ransom money. A search of his home revealed two hand saws, either of which fit exactly the scratch marks left on the ladder, a 63.5 mm hand plane with unique nicks that matched marks left on the ladder rungs (Figure 8), and nails identical to those used in the construction of the ladder. Perhaps the most interesting piece of evidence, however, was the missing floorboard in Hauptmann's attic. Koehler showed that one of the ladder rails was sawn from the attic floorboard (Figure 9). Not only did the type of nail and nail holes match, but the comparative anatomy showed that the growth rings and general grain pattern were a certain match. For a detailed description of the history and techniques used in the case, see Christensen (1977 and personal communication), Koehler (1937), Palenik (1982), Radin (1950), and Waller (1961).

Koehler used comparative anatomy to identify the wood. He found tool marks, physical matches with nail holes, and similar growth patterns on the ends of two boards. Most often, comparative anatomy uses patterns produced by growth rings, decay, defects, and abnormal growth. In north temperate regions, many trees have growth rings that are the same as annual rings; that is, each year the tree lays down another layer of growth. A count of the number of rings from pith to bark reveals the age of the tree, but the width of the ring and location of other defects or abnormal growth may help unravel a mystery. A few case examples help illustrate the use of growth patterns in forensic work.

In the Case of the Missing Logs, a farmer had logged off a number of acres of land and had stacked the logs neatly in the woods ready for shipment. That night, someone took the logs. The sheriff was called, and he started searching for the stack of logs. As he was driving around the area, he spotted a stack of logs on some other property. The ends of several logs were photographed, but one photograph in particular was unusual (Figure 10). It showed the butt log of a tree that had a rotten center, growth defects, chainsaw marks, and hinge (the area left uncut as the tree was felled). The sheriff then went to the logged area and found the matching stump.

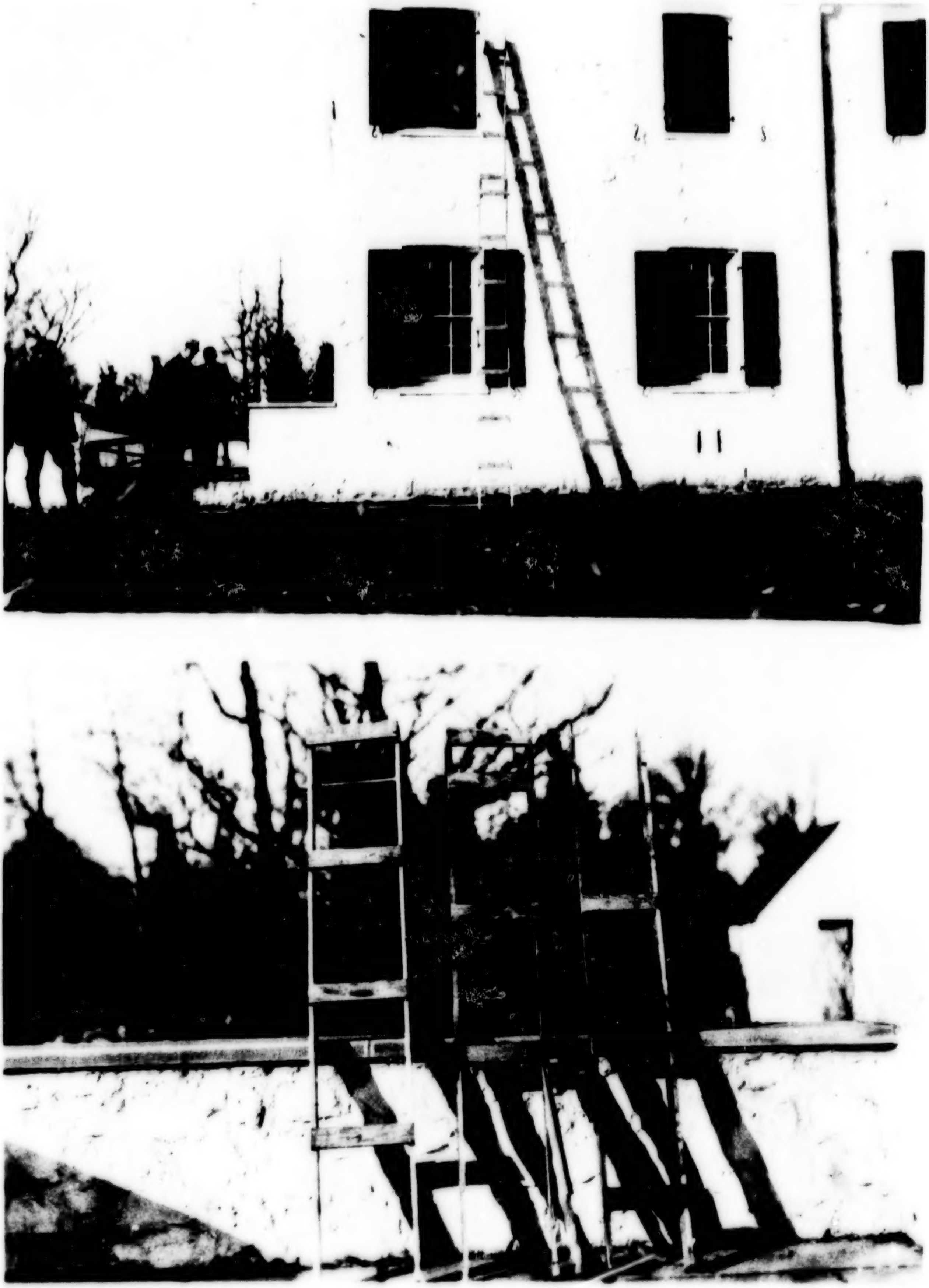


Figure 7. Ladder found at scene of Lindbergh kidnapping (upper) and disassembled (below) for easy transport in a car.

On a macroscopic level, the rotten center, growth defects, and hinge all matched perfectly; at higher magnification, the growth rings and chainsaw marks matched (Figure 11).

In another case, a skeleton was found beneath a small cucumber tree (*Magnolia acuminata*); a piece of shirt sleeve was found tied around the tree trunk approximately 6 m above the ground. It was assumed that the man hung himself or was hung by others. The man was not identified and the year of death was uncertain. A complete cross-section of the tree trunk was removed and sent to FPL for examination. By carefully following the constricted growth rings near the area with the sleeve, we concluded that the man had died approximately 5 years earlier. We also explained a plausible way the man could have hung himself. The man could have climbed the tree, tied the sleeve around his neck and the tree trunk, and then released his grip. The weight of the body would have bent the tree to within a few meters (feet) of the ground, or perhaps the tree was initially bent and upon release, the tree sprang back and strangled the man. Once the body decayed and fell from the shirt sleeve, the tree straightened and continued to grow with the sleeve attached.

In a similar case, the name and date "Ted Bundy 78" was found carved in a living aspen tree (*Populus* spp.) in the mountains of Utah (Figure 12). This caused quite a furor because Ted Bundy was suspected of killing a young girl in a National Park not far from where the tree was found. The girl's body was never found and the public demanded a search of the area for the missing body. The police wanted to know if FPL could tell when the carving was made. We received a slice from the tree trunk with a piece of the carved letters T, E, and D. We soon discovered that the carving did not penetrate the xylem (wood) or disturb the cambium, the layer of cells that divide to produce bark and wood cells. Thus, no marker or indicator was present to use as a reference point to count growth rings. At this point, I collaborated with Dr. Ray Evert, who is an expert in bark anatomy. We examined normal areas of bark, wound or carved areas, and areas away from the wound but in proximity. We discovered that the wound caused a layer in the bark (called the periderm) to begin forming successive annual layers of what we termed 'wound' periderm. As we examined the areas nearer the wound, we saw that the wound periderm divided (Figure 13). We examined several areas and found that the maximum number of wound periderms was eight. Thus, 8 years had passed since the carving. As a result of this work, the police could show that Ted Bundy did not make these carvings since he was incarcerated at the time.

Wood Identification

Wood identification is often coupled with comparative anatomy. In all of the previous cases cited, the wood involved was identified, but the identification was not really critical to solving the crime. In many cases, however, identification is the only option and comparative anatomy does not play a role.

In breaking-and-entering cases, robberies, murders, and other types of crimes, wood fragments can become trace evidence. Doors, windows, walls, ceilings, or other wooden objects at the scene of the crime are broken or used as weapons. In the process, wood fragments get attached or linked to the perpetrators or victims. These fragments can often be identified and linked to standards from the crime scene. In one case, sweepings from suspects revealed several very small wood fragments. One was thin-sectioned by hand, and the other two fragments were so small that they were placed directly on a slide and examined under the light microscope. One piece was a species in the white pine group (*Pinus* spp.), another a species of maple (*Acer* spp.), and the third a species of basswood (*Tilia* spp.). All three pieces were part of a ceiling that the suspects broke through to gain access. In two separate murder cases, pool cues were

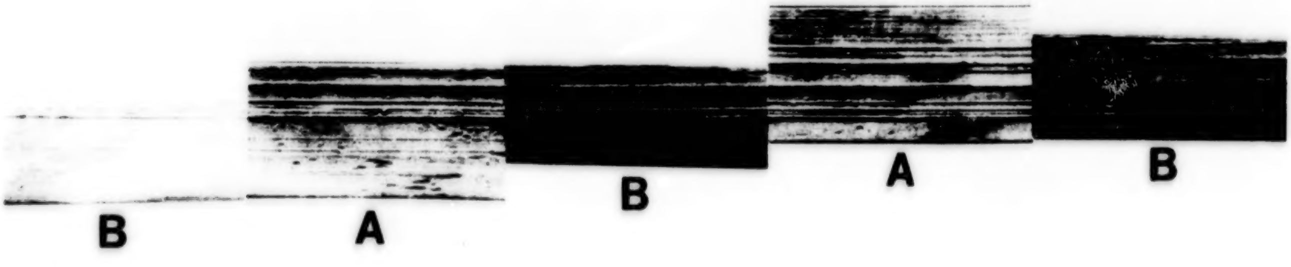


Figure 8. Unique pattern of ridges left by nicks on freshly planed pine (A) and nicks found on kidnapping ladder (B).

used as weapons. Wood fragments were found imbedded in the victim and on the suspect. In both cases, the cues were made from tropical woods that are not commonly found in the market place.

Sometimes an exact identification is not necessary, as in the case of the explosive from Central America. The wood filler or sawdust used in bombs confiscated in Central America was examined to see if the bombs were made outside Central America. The theory was that wherever the bombs were made, local sawdust would be used. The fragments were so small that they could not be sectioned (Figure 14). I examined the fragments under a light microscope, looking for anything that I could recognize as a species of north temperate origin (Figure 15). I was unable to identify the species of any fragments, but I concluded that the wood filler was probably tropical in origin. I was able to make that statement because the fragments did not have spiral thickenings, a feature common to many north temperate species. In addition, almost all the fragments were hardwoods (Figure 15). This is expected of tropical sawdust because most trees in the tropics are hardwoods; in the north temperate regions, softwoods are much more common. The only softwood fragment closely resembled a species of *Podocarpus*, one of the few softwoods confined to the tropical regions (Figure 16). I also found a fragment from a monocot (perhaps a palm), several fragments that contained a large amount of prismatic crystals in axial parenchyma cells (Figure 17), and a fragment with small parenchyma cells or chambered cells. These features are fairly common in some tropical species, but they are rare in north temperate species.

In some cases, both identification and comparative anatomy are combined. The following is a case that involved several aspects of wood anatomy and related fields.

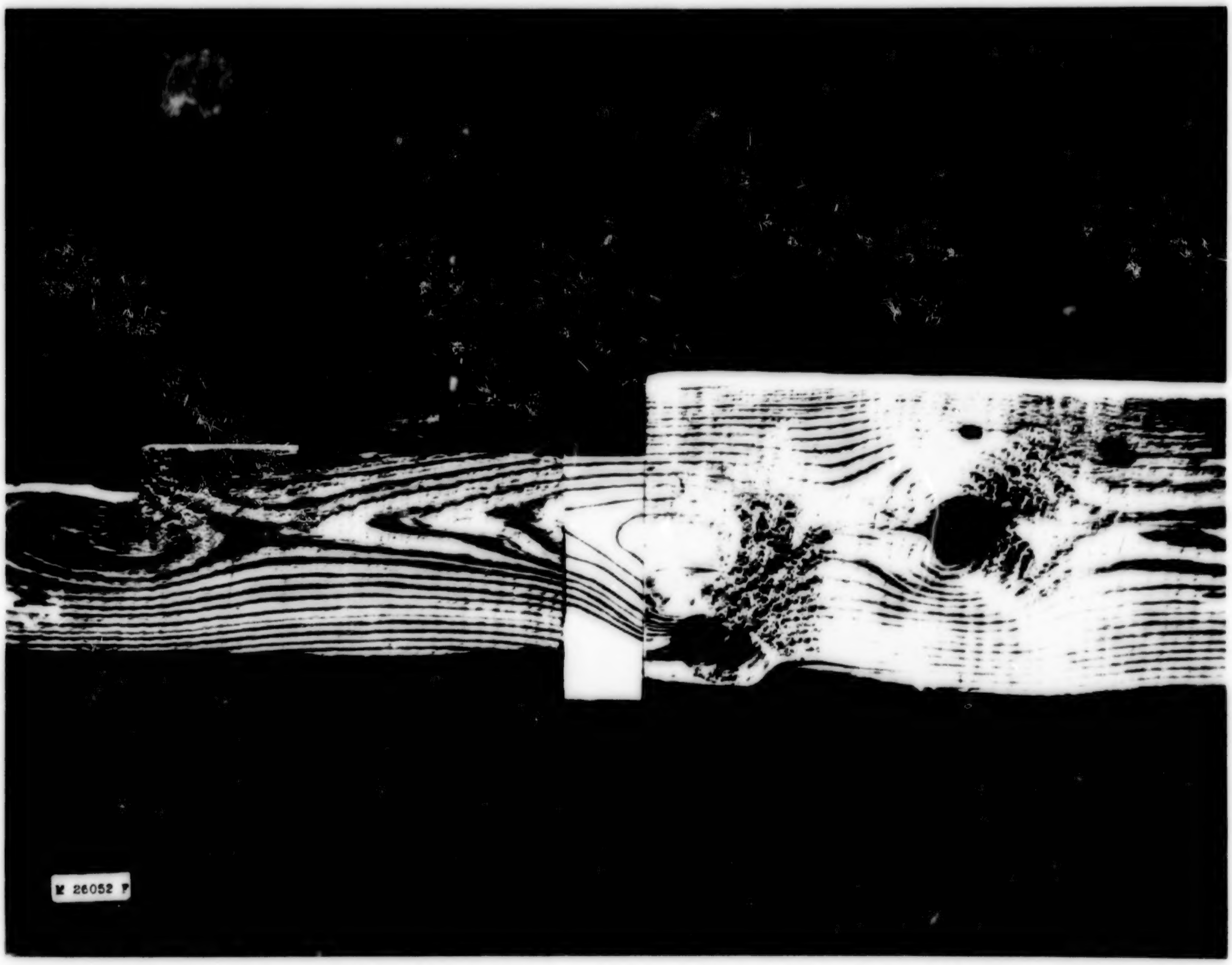


Figure 9. Matched halves of ladder rail 16 swan from attic floorboard. Although a 35-mm piece of wood was missing, Koehler showed that the two halves matched perfectly. The annual rings were identical in number, curvature, width, and prominence, and the grain pattern was the same. Drawing depicts the missing piece.

In the Case of the Red Paint Chip, a murder had taken place in Georgia. The victim was found in the woods covered with nearby debris. The debris included chairs, rugs, cushions, and two red painted posts. This area was used by hunters, who apparently brought the items and left them there. The red posts, however, were thought to belong to the suspect, the husband of the victim, because (1) the victim's son said that the red posts were stored in the house, (2) the son had seen them in his father's pickup truck, and (3) the husband admitted at one time that the red posts were in his pickup. In the victim's home, under the stairs where the red posts had apparently been stored, a red paint smudge was found on a piece of yellow pine (Pinus spp.) 2 by 4 lumber. This red paint was compared to the red paint on the post, and a good match was noted in gross structure and chemical analysis. The forensic scientist in charge noted that a few fibers were clinging to the back of the red paint (Figure 18).

I was asked to examine these fibers to determine whether they were conifer fibers from the yellow pine lumber or fibers from the red painted posts, which were identified as a species in the white oak group (*Quercus* spp.). The cells in Figure 19 are ray cells and fibers. The ray cells did not have any cross-field pitting and no ray tracheids were evident, suggesting that they were hardwood ray cells and not rays from some conifer. The fibers were of two types: pointed thick-walled fibers and long, broad, thin-walled fibers. Fibers of two distinct types do not occur in conifers, but they do occur in some hardwoods. I concluded that the fibers were libriform fibers and vasicentric tracheids that are typical of oak. Under high magnification and polarized light (Figure 20), the fibers from the red paint chips appeared to have large slit-like structures that initially were thought to be pits. Upon closer scrutiny, however, these slit-like structures were found to be openings caused by decay fungi. This decay pattern was found both in the fibers clinging

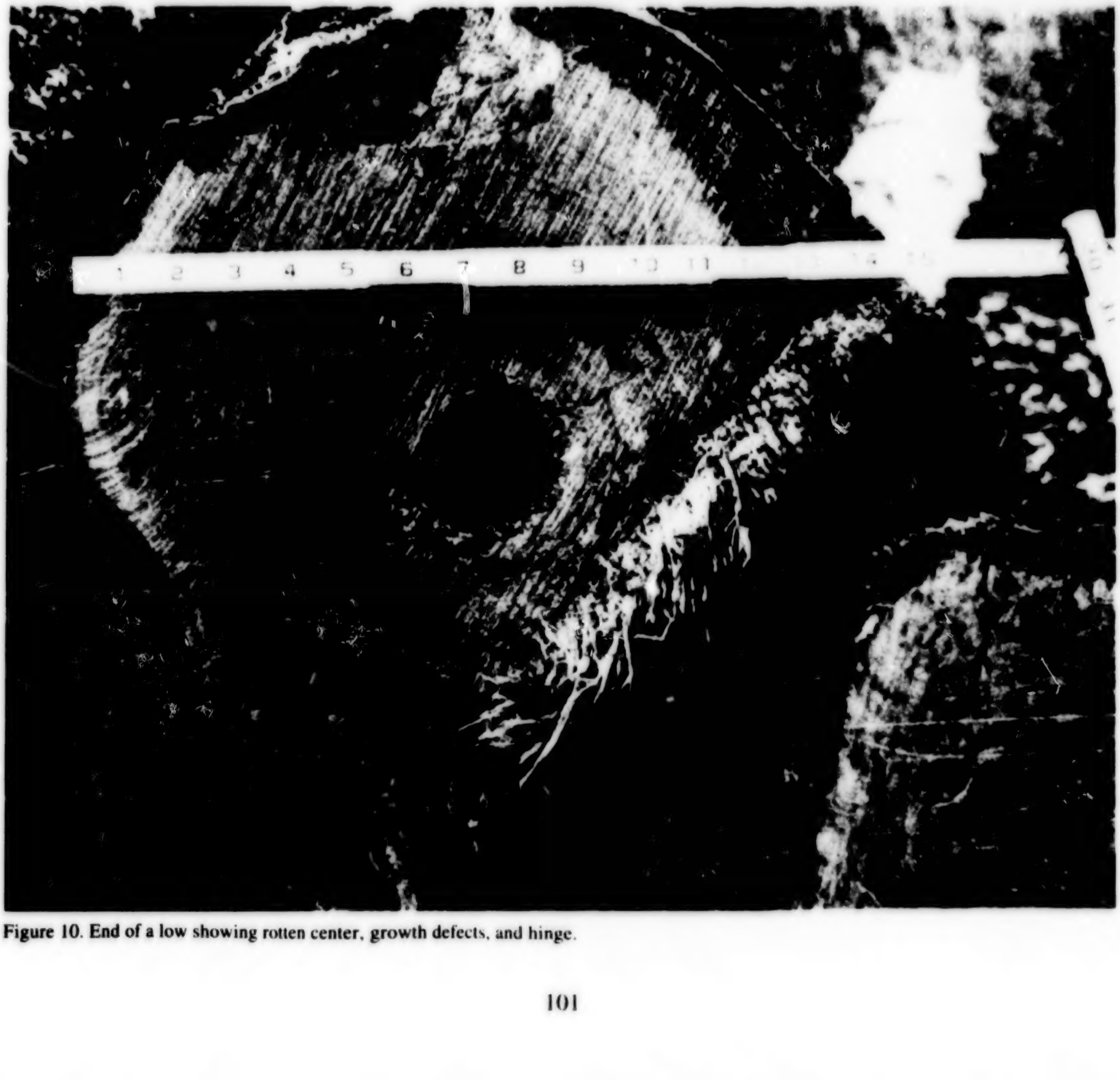


Figure 10. End of a low showing rotten center, growth defects, and hinge.

to the red paint chips and the white oak posts. Not only was the decay pattern the same, but also the type of fungi. This case used both identification and comparative anatomy to show that the red paint chips found on the stairs did come from the red painted posts found at the scene of the crime.

CONCLUDING REMARKS

Comparative wood anatomy and wood identification can play an important role in forensic science. When gathering trace evidence, do not ignore wood fragments. They could contain clues that help solve the crime.

REFERENCES

Brazier, J.D. and Franklin, G.L. (1961). Identification of hardwoods: A microscope key, Forest Products Research Bulletin No. 46, Her Majesty's Stationery Office, London.

Carlquist, S. (1988). Comparative Wood Anatomy, Springer- Verlag, NY.

Christensen, D. J. (1977). Lindbergh kidnapping - The ladder link, Forest and People 27(4):8-11.

Core, H. A., Cote, W. A. and Day, A. C. (1979). Wood Structure and Identification, 2nd ed, Syracuse University Press, Syracuse, New York.

Edlin, H. L. (1977). What Wood Is That? A Manual of Wood Identification, Stobart and Son Ltd., London.

Forest Products Laboratory. (1980). Structure of wood, USDA, Forest Service, Forest Products Laboratory Research Note FPL-04.

Grosser, D. (1977). Die Holzer Mitteleuropas, Springer-Verlag, NY.

Hoadley, R. B. (1980). Understanding Wood: A Craftsmen's Guide to Wood Technology, Tauton Press, Newton, CT.

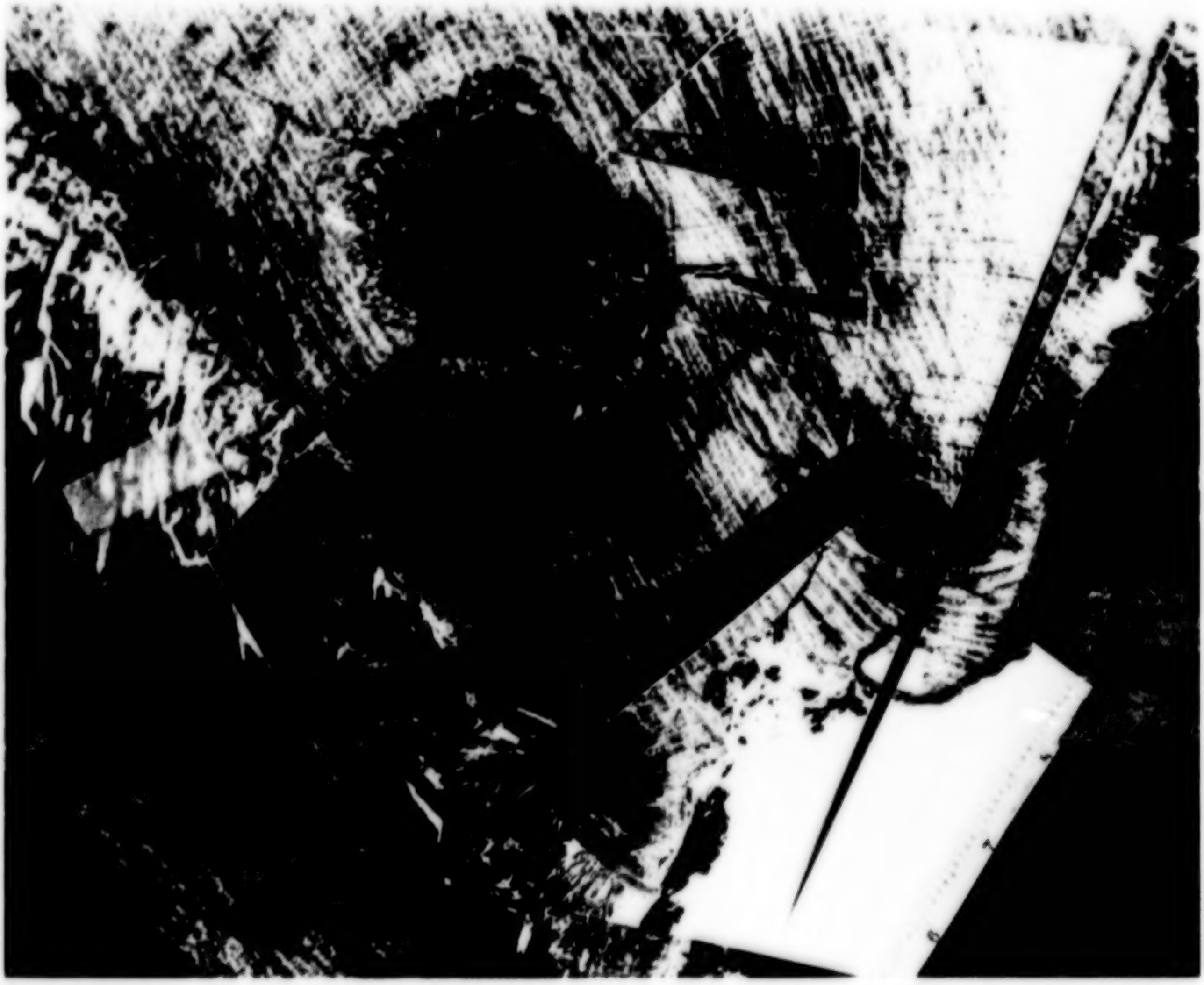


Figure 11. Log shown in Figure 10 at higher magnification and overlaid with pieces of photo from stump to show exact match in rotten center, growth defects, and hinge.

Figure 12. Section of tree trunk with the inscription "TED BUNDY 78."

Hoadley, R. B. (1990). Identifying Wood: Accurate Results With Simple Tools, Tauton Press, Newton, CT.

IAWA Committee. (1989). IAWA list of microscopic features for hardwood identification, IAWA Bull. n.s. 10(3):219-332.

Ilic, J. (1987). The CSIRO family key for hardwood identification, Tech. Paper No. 8., Div. of Chemistry and Wood Technology, Commonwealth Scientific and Industrial Research Organization, Australia.

Ilic, J. (1990). The CSIRO macro key for hardwood identification, Tech. Paper No. 8., Div. of Forestry and Forest Products, Commonwealth Scientific and Industrial Research Organization, Australia.

Koehler, A. (1937). Techniques used in tracing the Lindbergh kidnapping ladder, Am. J. Police Sci. 27:5.

Kribs, D. A. (1968). Commercial Foreign Woods on the American Market, Dover Publishers, NY.

Kukachka, B. F. (1960). Identification of coniferous woods, TAPPI 43(11):887-896.

Kukachka, B. F. and Miller, R. B. (1980). A chemical spot-test for aluminum and its value in wood identification, IAWA Bull. n.s. 1:104-109.

Metcalfe, C. R. and Chalk, L. (1950). Anatomy of the Dicotyledons, Vols. 1 and 2., Clarendon Press, Oxford.

Metcalfe, C. R. and Chalk, L. (1979). Anatomy of the Dicotyledons, 2nd ed., Vol. 1., Clarendon Press, Oxford.

Metcalfe, C. R. and Chalk, L. (1983). Anatomy of the Dicotyledons, 2nd ed., Vol. 2., Clarendon Press, Oxford.

Metcalfe, C. R. (1987). Anatomy of the Dicotylendons, 2nd ed., Vol. 3., Clarendon Press, Oxford.

Miles, A. (1978). Photomicrographs of world woods, Building Research Establishment Report, Her Majesty's Stationery Office, London.

Miller, R. B. (1981). Explanation of coding procedure, IAWA Bull. n.s. 2:111-145.

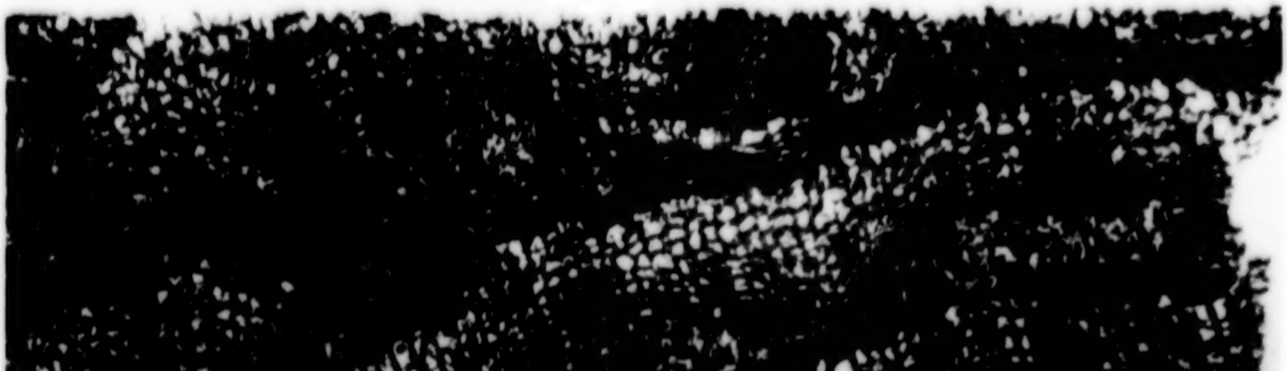


Figure 13. Eight annual layers of "wound periderm" near the carved name.

Figure 14. Very small wood fragments from explosives confiscated in Central America.

Miller, R. B., Quirk, J. T. and Christensen, D. J. (1985). Identifying white oak logs with sodium nitrite, Forest Prod. J. 35:33-38.

Palenik, S. (1982). Microscopic trace evidence - the overlooked clue, Part IV, Arthur Koehler - Wood detective, The Microscope 31:1-14.

Panshin, A. J. and deZeeuw, C. (1980). Textbook of wood technology, 4th ed., McGraw-Hill Book Co., NY.

Phillips, E. W. J. (1979). Identification of softwoods by their microscopic structure, Forest Products Research Bulletin No. 22, Her Majesty's Stationery Office, London.

Radin, E. D. (1950). Sawdust trail, In: 12 Against Crime, (Radin, E.D., ed.), G. P. Putnam's Sons, NY.

Raven, P. H., Evert, R. V. and Eichhorn, S. E. (1986). Biology of Plants, 4th ed., Worth Publishers, NY.

Schweingruber, F. H. (1990). Anatomie Europaischer Holzer — Anatomy of European Woods, Paul Haupt Berne and Stuttgart Publishers, Zurich.

Waller, G. (1961). Kidnap: The Story of the Lindbergh Case, Dial Press, NY.

Wheeler, E. A., Pearson, R. G., LaPasha, C. A., Zack, T. and Hatley, W. (1986). Computer-aided wood identification, North Carolina Agriculture Research Service Bulletin, No. 474, North Carolina State University, Raleigh, NC.

White, M. S. (1980). Wood Identification Handbook: Commercial Woods of the United States, Charles Scribner's Sons, NY.

Figure 15. Fragments from explosives viewed with low magnification under a light microscope.

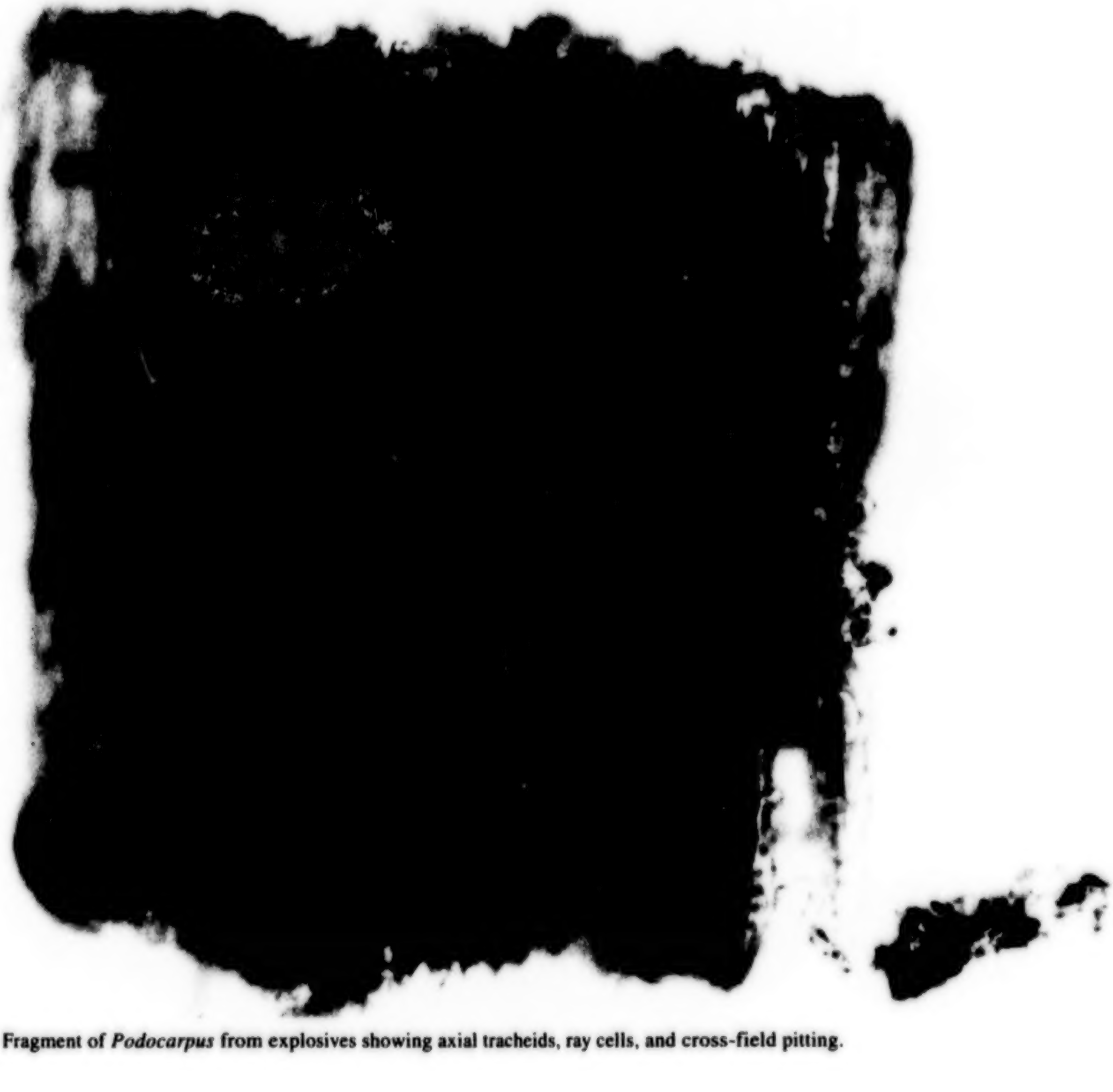


Figure 16. Fragment of *Podocarpus* from explosives showing axial tracheids, ray cells, and cross-field pitting.

Figure 17. Fragment of tropical hardwood from explosives showing prismatic crystals in axial parenchyma cells.

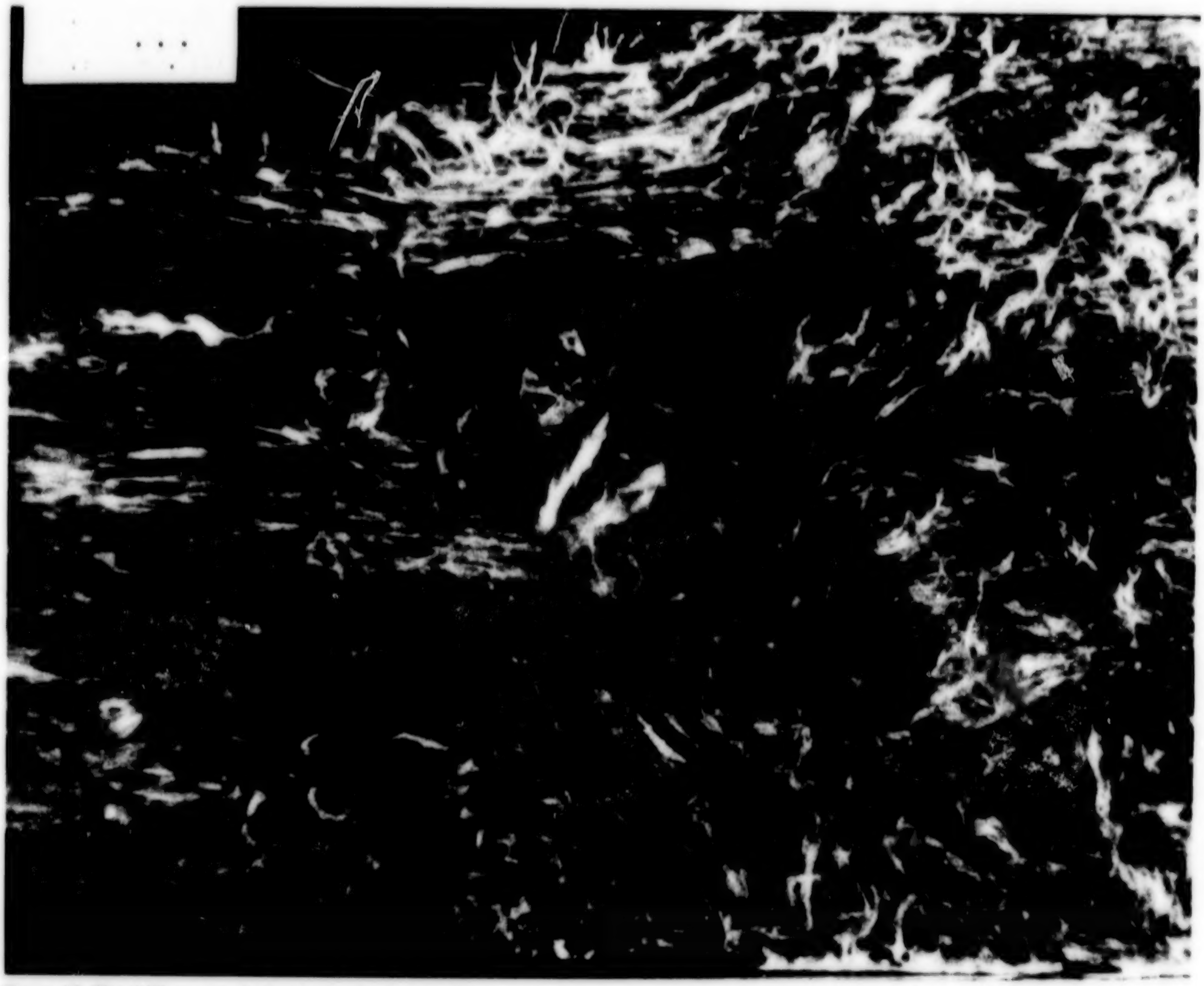
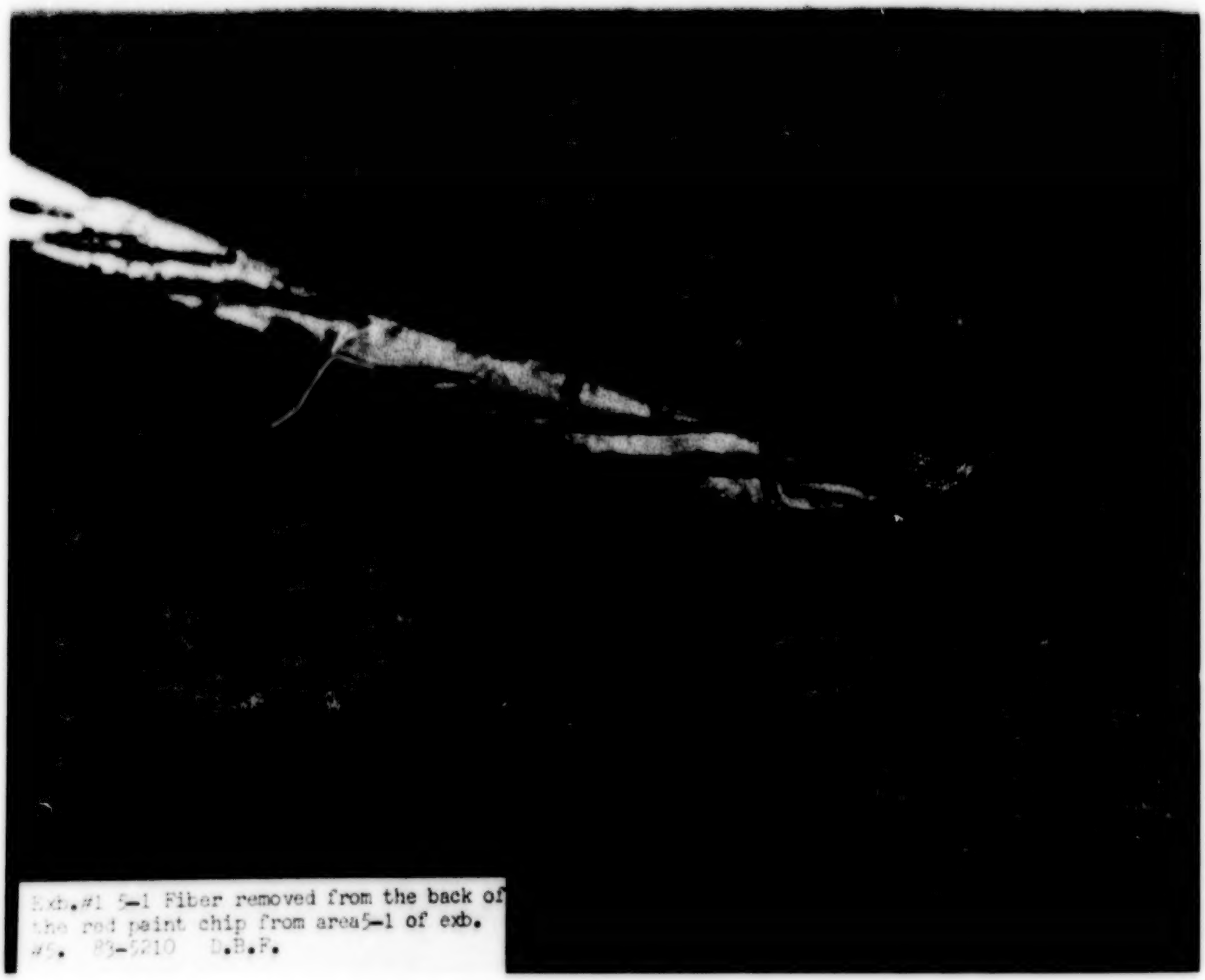


Figure 18. Wood fibers attached to back of red paint chip.

Figure 19. Ray cells, libriform fibers, and tracheids from back of red paint chip.



Exb.#1 5-1 Fiber removed from the back of
the red paint chip from area5-1 of exb.
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Figure 20. Wood fiber from back of red pain chip, showing slit-like structures and fungal hyphae.

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ENTOMOTOXICOLOGY: USE OF INSECTS AS TOXICOLOGICAL INDICATORS — RECENT ADVANCES

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Over the past several years, there has been an apparent increase in drug-related deaths reported in the United States. These deaths are, in many instances, not discovered for a period of several days and, as a result of the processes of decomposition, estimates of postmortem intervals are made using entomological data. The data most frequently employed are those associated with insect developmental rates and succession patterns (Goff and Odom 1987; Goff and Flynn 1991; Lord *et al.* 1986). Until recently, the accuracy of these estimates in deaths involving narcotic intoxication has been subject to question and no studies existed detailing the effects of drugs from decomposing tissues, such as cocaine or heroin, on the rates of development of carrion feeding insects. Additionally, there were few data dealing with the effects of other tissue contaminants, such as toxins or environmental pollutants, in decomposing tissues on the rates and/or developmental patterns of insects using such tissues as food sources. Interest has also recently focused on the potential use of carrion insects as alternate toxicological specimens in situations where traditional toxicological specimens, such as blood, urine or solid tissues are unavailable.

INSECT LIFE CYCLES

With relatively few exceptions, adult insects lay eggs. The immature forms of some species closely resemble the adult insect, generally lacking only wings. These immatures, termed nymphs, periodically cast their skins as they increase in size, eventually displaying all of the characters of the adult. Most insects of forensic importance, however, pass through three dissimilar stages during their development (egg, larva and pupa) before reaching the adult stage. None of these developmental stages resembles the adult and the food sources consumed differ from those used by the adult insect. The insects most frequently involved in estimations of postmortem interval during the first four weeks of decomposition are the true flies, or Diptera, and these are also the taxa most frequently used in drug-related analyses. The predominant species encountered are: the calliphoridae or blow flies, and Sarcophagidae or flesh flies.

Both the Calliphoridae and Sarcophagidae are highly mobile, strong flying species. These flies are typically the first insects to arrive at a corpse. Under tropical conditions in the Hawaiian Islands, Calliphoridae may arrive within minutes following death. In temperate situations, their arrival may require several hours or days depending on habitat, environmental conditions and other factors. Adult flies will either begin to lay eggs (oviposit) immediately or feed on the various protein-rich fluids seeping from the corpse and then begin oviposition. On corpses which have not suffered traumatic injury, the initial sites for oviposition will generally be the natural body openings (eyes, ears, nose, mouth, nose, and, if exposed, anus and genitals). Wounds or blood may provide preferential sites attractive for oviposition, although this attraction may vary depending on the species of fly and degree of injury.

Blow fly eggs are small (2-3 mm), elongate, and white to yellow in color. They are typically laid in large clusters and, during warmer periods of the year, may completely fill natural body openings and wound sites (Figure 1). During cooler periods, when adult fly populations are lower, the eggs may be few in number and more difficult to locate, being hidden in cryptic sites such as the inside of the nose or behind the eyelids. Typically the egg stage for blow flies lasts from 1 to 3 days.

When the eggs hatch they produce larvae, commonly referred to as maggots. These are small, somewhat peg-shaped organisms (Figure 2). The anterior end has a pair of mouthhooks which are used in both feeding and locomotion. The posterior end bears a pair of flattened spiracles through which the maggot breathes (Figure 3). These features, along with size and shape, provide important characters for identification. Maggots

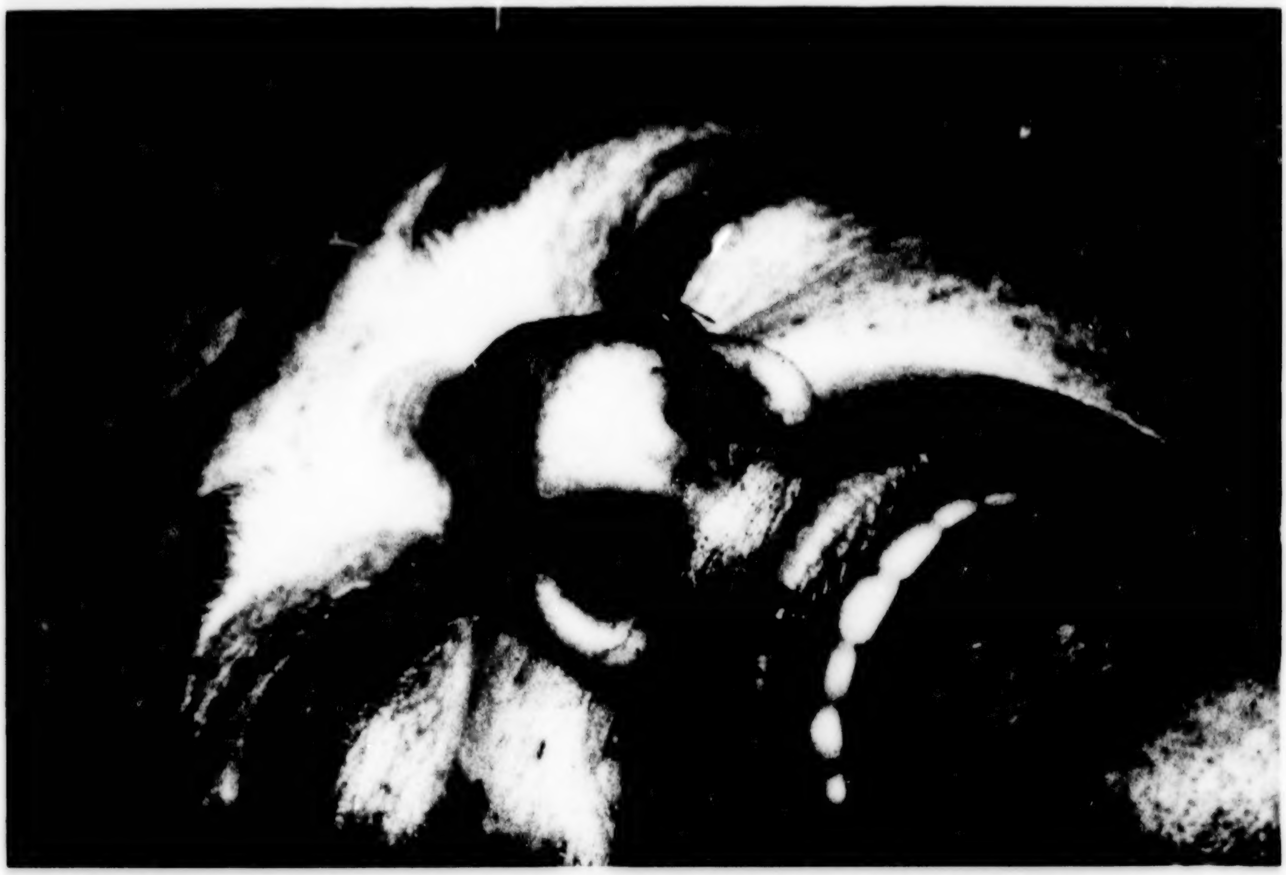

Figure 1. Blow fly eggs are typically laid in large clusters and, during warmer periods of the year, may completely fill natural body openings and wound sites.

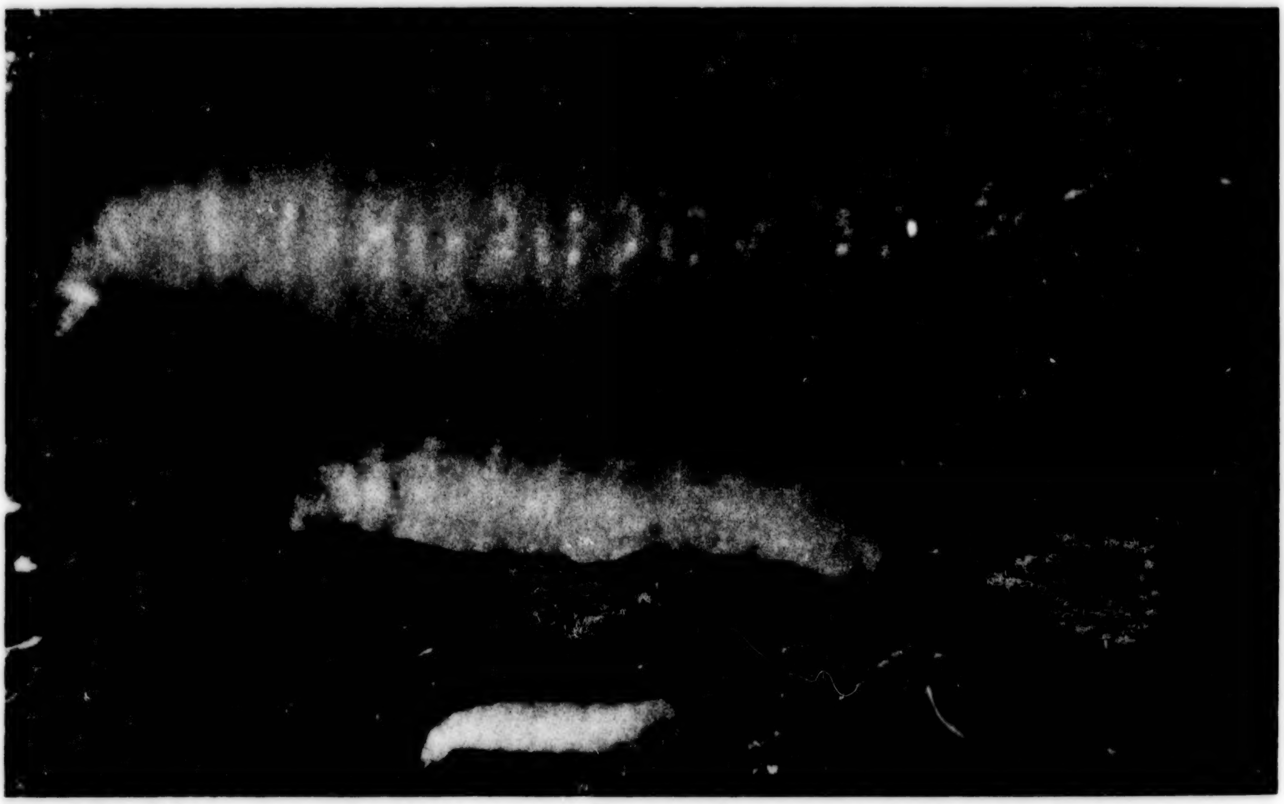

Figure 2. Blow fly larvae are commonly referred to as maggots. These are small, somewhat peg-shaped organisms. The maggots grow rapidly passing through 3 instars before reaching maturity.

Figure 3. The Blow fly larva's posterior end bears a pair of flattened spiracles through which the maggot breathes.

grow rapidly, passing through 3 stages (Figure 2) (instars) before reaching full size. The eggs laid on a corpse will typically hatch at the same time, resulting in a mass of maggots which move about the corpse feeding as a group. This group feeding behavior results in the dissemination of bacteria and production of digestive enzymes which enable the maggots to consume most of the soft tissues of the corpse in a highly efficient manner. Maximum size will be reached in a period varying from several days to weeks, depending on the species involved, numbers of maggots present, and environmental conditions.

After reaching maximum size maggots undergo a dramatic change in behavior. Feeding ceases and the maggots begin to migrate away from the corpse. This migration is typically to a drier habitat where the maggots burrow into the substrate and begin the process of pupation. During pupation, the outer skin of the maggot becomes hardened and forms a protective cover. This reddish to dark brown pupa somewhat resembles a small football (Figure 4). Within this protective case, the maggot undergoes a reorganization and eventually emerges as an adult fly. The period of time required for this transformation varies depending on the species of fly and environmental factors, particularly temperature. The pupal case itself is quite resistant to environmental degradation and may be found in the soil under the corpse for hundreds of years. Blow fly pupal cases can supply valuable forensic information long after the remains have decomposed (Nuorteva 1987).

The life cycle for the Sarcophagidae or flesh flies is quite similar to that of the blow flies, with one important difference. Flesh flies associated with decomposing remains do not lay eggs (oviposit) but rather deposit 1st instar larvae (larviposition) on remains. This process requires that the developing larva (maggot) be retained in the body of the adult female fly longer than for an egg. Thus, numbers of larvae produced per female are lower for Sarcophagidae than for Calliphoridae. In total numbers of maggots present on the corpse, generally the Sarcophagidae are far outnumbered by the Calliphoridae. There are exceptions to this in specialized circumstances, as may occur in corpses found indoors (Goff 1991) or exposed to severe environmental conditions.

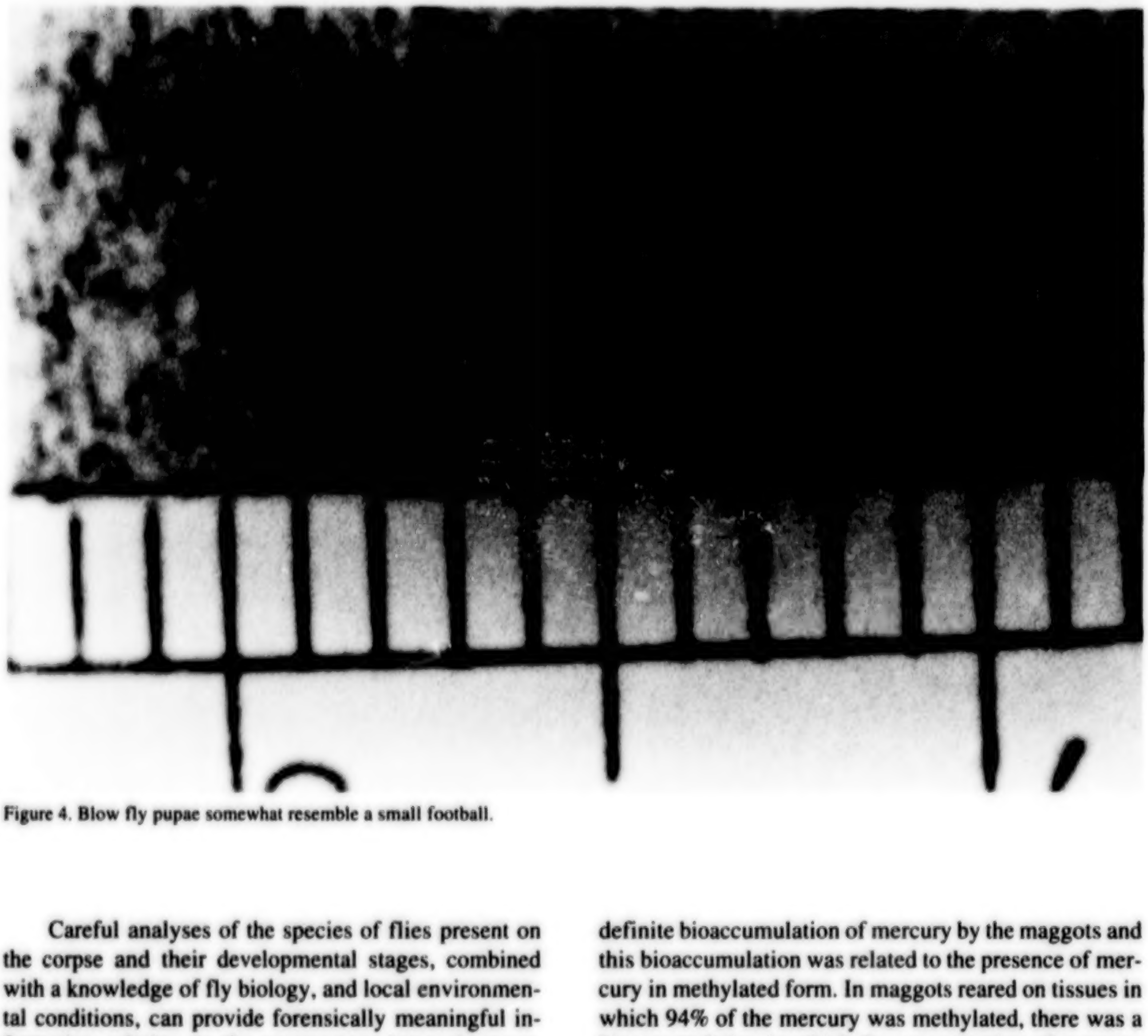

Figure 4. Blow fly pupae somewhat resemble a small football.

Careful analyses of the species of flies present on the corpse and their developmental stages, combined with a knowledge of fly biology, and local environmental conditions, can provide forensically meaningful information relating to the postmortem interval, movement of the corpse after death from one locality to another, manner of death, and, as will be discussed here, drugs and/or toxins present in the corpse.

DETECTION OF TOXINS AND DRUGS

There are several publications detailing the detection of various toxic and controlled substances through the analyses of arthropods. In these reports, the arthropods have generally been homogenized and then processed in the same manner as other toxicological tissues or fluids. Analytic procedures have included RIA techniques, gas-chromatography, and thin-layer chromatography.

Nuorteva and Nuorteva (1982) detailed the recovery of mercury from various species of calliphorid maggots fed on fish containing known concentrations of mercury. In this study, it was noted that there was a definite bioaccumulation of mercury by the maggots and this bioaccumulation was related to the presence of mercury in methylated form. In maggots reared on tissues in which 94% of the mercury was methylated, there was a bioaccumulation in which the concentration of mercury in the maggots was 4.3 times greater than that in the tissues. In fish containing lesser amounts of methylated mercury, the concentration detected in maggots was only 1.5 times greater than that in tissues. The mercury ingested by maggots was retained through the pupal stage and detectable in emerging adult flies. Once the adult stage was reached, mercury was rapidly eliminated. After 2 days the adult flies contained only 50% of the original mercury levels. A more detailed analysis revealed that, for the most part, excretion actually occurred during the pupal stage where accumulated mercury was secreted into the meconium of the hindgut (Nuorteva and Nuorteva 1982). During these studies, no ill effects were generally exhibited by the adult flies or maggots, although some individuals were observed having difficulty in pupation. Maggots which had fed on tissues containing mercury were fed to the staphylinid beetle *Creophilus maxillosus* and a secondary bioaccumulation was noted in these predatory beetles. While no ill effects were observed for C. maxillosus, subsequent work by Schott and Nuorteva (1983) showed a decrease in activity for the tenebrionid beetle *Tenebrio mollitor* fed on dried maggots with a high mercury content. Nuorteva and Nuorteva (1982) had previously noted the occurrence of "Minimata-like symptoms" (consisting of irregularities in motor control and muscular coordination) for adults of that species fed on mercury-containing maggots. No change in life span was noted for the beetles fed on mercury-containing maggots in either study.

In a similar manner, Sohal and Lamb (1977, 1979) demonstrated the accumulation of various metals, including copper, iron, zinc, and calcium, in tissues of adult houseflies, Musca domestica. As with the mercury studies cited, no detrimental effects to the adult flies were associated with the bioaccumulation of these metals.

One example of an application of these types of data was given in a case presented by Nuorteva (1977). In this instance adult flies reared from a badly decomposed, unidentified female discovered in the rural area of Inkoo, Finland, were analyzed for mercury content in an attempt to determine the geographic origin of the victim. The low mercury content of the adult flies on emergence (0.12-0.15 ppm) indicated that the individual came from an area relatively free from mercury pollution. When the individual was identified, she proved to have been a student from the city of Turku, an area free from mercury pollution.

Utsumi (1958) observed that rat carcasses varied in their attractiveness to flies depending on the poison causing death. This research did not, however, include any attempt to detect the toxins in the maggots which eventually developed on the rat carrion. Leclercq and Brahy (1990) note the detection of arsenic poisoning through the analyses of species of Piophilidae, *Fannia*, and Psychodidae in a case from France.

Detection of an organophosphate insecticide, malathion, was reported by Gunatilake and Goff (1989). In this instance, a 58-year-old male with a previous history of suicide attempts was discovered in the crawlspace under his mother's home in Honolulu. Adjacent to the remains was a bottle of Malathion-50 with approximately 177 ml missing. Both tissues and maggots of 2 species of Calliphoridae were analyzed for malathion using gas-chromatography. The fat tissues from the corpse had malathion detected at 17 mg/kg. The combined sample of the maggots of *Chrysomya megacephala* and *Chrysomya rufifacies* showed malathion at a concentration of 2050 µg/g. It is of significance that the developmental stages of both species of *Chrysomya* in this case were indicative of a postmortem interval of 5 days. The individual had last been seen alive 8 days prior to the discovery of the corpse. It is possible that the presence of malathion in the tissues of the corpse may have served to delay oviposition for a period of several days. This is supported by the presence of only 2 species of flies on the corpse. In outdoor situations in the Hawaiian Islands, a far greater number of insect species should have been present on the corpse at either a 5 or 8 day interval. Typically, other species of flies and predatory Coleoptera in the families Staphylinidae and Histeridae would have been expected to have invaded the corpse and the surrounding substrate.

Beyer *et al.* (1980) detailed the case of a 22-year-old female whose decomposed remains were discovered 14 days after she had last been seen alive. The individual had a previous history of 5 suicide attempts. An empty bottle from a prescription for 100 tablets of phenobarbital, filled 2 days before she was last seen alive, was found in a purse adjacent to the remains. As there were no tissues on the almost completely skeletonized body available for analysis, larvae of the calliphorid *Cochliomyia macellaria*, feeding on the remains, were collected and analyzed for drug content. Phenobarbital was detected by gas-chromatography and confirmed by thin layer chromatography at a concentration of 100 µg/g.

Kintz *et al.* (1990a,b) have detailed further detections of prescription drugs through analyses of maggots. In one case, the subject was a male with a determined postmortem interval of 67 days. There were identifiable organs present for toxicologic analyses using liquid chromatography. These included heart, liver, lung, spleen, and kidney, in addition to bile. Calliphorid maggots were also collected and analyzed. Results of analyses showed 5 drugs present in the maggots as well as in bile, heart, liver and lung (triazolam, oxazepam, phenobarbital, alimemazine, and clomipramine). Triazolam was not detected in the spleen and kidney, although the other drugs were present. In this case, it was not possible to establish any correlations between the concentrations of drugs in the larvae and the human tissues. It is of interest to note that Kint *et al.* (1990a,b) observed fewer endogenous peaks in chromatograms obtained from maggot extractions than those from human tissues. Further evidence of the toxicological of insect specimens potential was provided by Kintz *et al.* (1990a,b) in which they were able to detect other drugs, bromazepam and levomepromzine, in maggots obtained from human remains.

Recent studies by Introna *et al.* (1990) detailed the results of analyses of maggots fed on liver tissues from 40 cases in which opiates had been detected at post mortem exam. In this study, opiates were effectively detected through analyses of maggots which had fed on opiate contaminated tissues using RIA techniques. A significant correlation between the concentrations of opiates in the liver tissues and the paired maggots sampled was also observed. While the qualitative relationship was quite clear from their results, the quantitative relationship was less clear and more research in this area is suggested. Similar results were presented for qualitative detection by Goff *et al.* (1989) and Goff *et al.* (1991) for studies using known dosages of cocaine and heroin administered to rabbits.

Lord (1991) presents an account of the use of toxicological analysis of maggots to determine cocaine intoxication. In that case, the almost completely skeletonized remains of a 29-year-old male intravenous drug user were discovered in February, almost 5 months after he had last been seen alive. His girlfriend indicated that she believed he had used intravenous cocaine immediately prior to his disappearance. Associated with the remains were numerous maggots and pupae. Skeletal muscle along with maggots were submitted for toxicological analysis using gas-chromatography. Both tissues and maggots tested positive for cocaine and benzoylecognine. As in previous cases, the sample from the maggots had less interference from by-products of decomposition and provided more suitable samples for quantitation. The pupae and empty pupal cases were not tested for cocaine in this case, but were found suitable for analysis using extraction techniques developed for human hair. If cocaine or other drugs are deposited in the protein matrix of the pupal cases, toxicological analyses may be possible years after death. Cocaine and other drugs have been detected in the protein matrix of human hair (Graham *et al.* 1989, Baumgartner *et al.* 1989) and it is not unreasonable to suggest a similar situation may exist for pupal cases.

EFFECTS OF DRUGS IN TISSUES ON DEVELOPMENT OF INSECTS

While previously cited studies have documented the potential of maggots as alternate specimens for toxicological analyses, they have not addressed questions concerning the effects of these substances on the rate of insect development. In the estimation of the postmortem interval, particularly during the first 2-4 weeks of decomposition, it is assumed that the insects, particularly the Diptera, will develop at known, predictable rates for given climatic conditions. That this might not always be the case when drugs are involved was first demonstrated by Goff *et al.* (1989) during their studies on the effects of cocaine in decomposing tissues on the rate of development of the sarcophagid *Boettcherisca peregrina*. In this study, domestic rabbits were administered dosages calculated by weight to represent 0.5, 1.0, and 2.0 times median lethal dosages of cocaine. Those animals receiving the lethal dosages were allowed to expire as a result of the action of the drug and the animal receiving the sublethal dosage and control were sacrificed in a CO_2 chamber. Presence of cocaine and/or its major metabolite benzoylecognine were confirmed by analyses of samples of liver tissues. Livers and spleens were removed from animals following death and exposed to a colony of *Boettcherisca peregrina* for larviposition. Samples were measured from each colony at 6-hour intervals and samples of maggots removed at 24-hour intervals for drug analyses. Samples of maggots from all colonies feeding on tissues containing the cocaine and/or benzoylecognine were positive for the drug or metabolite. Control liver and maggots were negative for both substances. In this study, there were two patterns of development detected. The control and sublethal colonies developed at approximately the same rate, as indicated by the total length of the larvae measured. By contrast, beginning at hour 36, the 1.0 and 2.0 times median lethal dosage colonies developed more rapidly (Figure 5). There were significant differences detected ($P<0.05$) until hour 76. Pupation was first observed in the twice median lethal dosage colony, followed by the median lethal, sublethal and control colonies. No significant variation in length of the pupal period was observed (Table 1) and no differences in pupal mortality were detected. Adults from all colonies produced viable offspring when supplied with liver 13 days following eclosion of adults. The colonies were followed for four generations and no abnormalities were observed.

Similar studies were conducted by Goff *et al.* (1991) for maggots feeding on decomposing tissues containing heroin. As above, dosages were calculated based on weight to represent 0.50, 0.75, 1.00, and 2.00 times median lethal dosage. Rates of development as indicated by total length of maggots were not significantly different ($P<0.05$) until hour 18. At that point, maggots in all colonies fed on tissues containing heroin began to de-

Table 1. PUPAL DURATION AND ADULT EMERGENCE FOR COLONIES OF *B. PEREGRINA* REARED ON RABBIT LIVER TISSUE CONTAINING VARYING AMOUNTS OF COCAINE.

Colony	Total Pupae Obtained	Total Adults Emerging	% Emerging	$\bar{X}$ Duration in Hours of Pupal State (Range)
Control	459	416	91	255 (234 - 312)
35 mg	445	407	91	253 (234 - 300)
69 mg	390	359	92	261 (240 - 294)
137 mg	708	649	91	252 (228 - 294)

Reproduced from Goff *et al.* 1989, with permission of the Entomological Society of America.

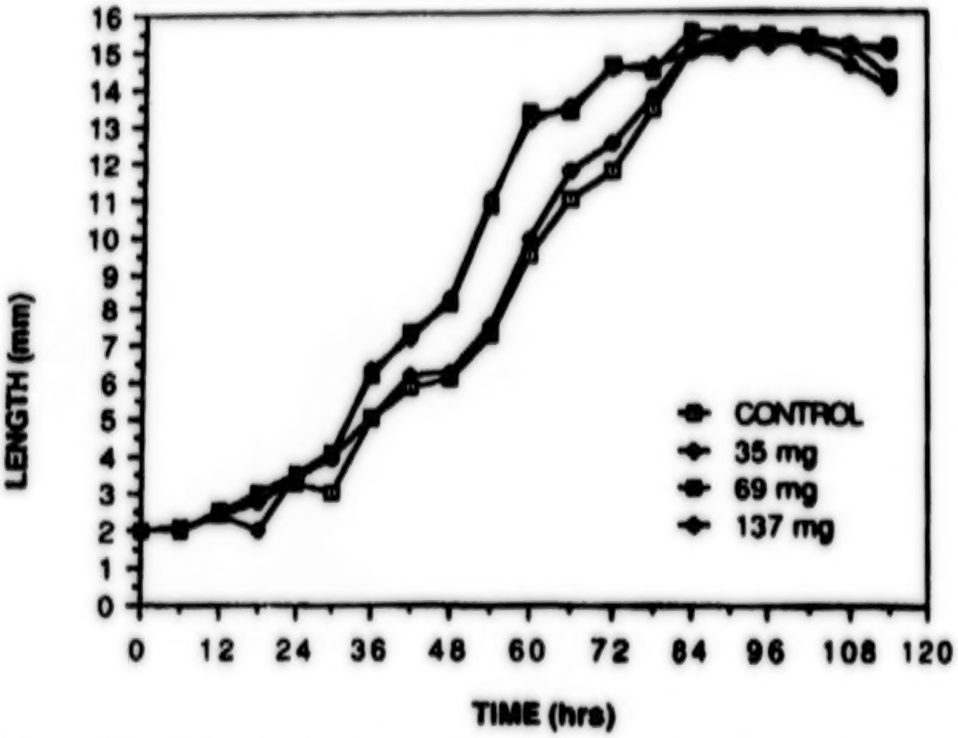

Figure 5. Rates of developmental, as indicated by total body length, of larvae of *B. peregrina* reared on tissues containing 35, 69 and 137 mg of cocaine. Reproduced from Goff *et al.* 1989, with permission of the Entomological Society of America.

velop at rates significantly greater than those observed in the control colony. These differences (Figures 6 and 7) continued through hour 96, when maximum larval lengths were recorded for maggots in all colonies. Maggots from all colonies fed on tissues containing heroin (as morphine) were significantly larger than maggots from the control colony ($P<0.05$). Duration of the puparial period was significantly longer for maggots from colonies fed on tissues containing heroin and was directly proportional to the concentration of the drug (as morphine) in the tissues (Table 2). This study has indicated that an estimate of the postmortem interval based on normal development of B. peregrina could have an error of up to 29 hours, if based on the larval stage, and 18-38 hours, if based on the pupal stage.

Studies are currently being conducted in the Forensic Entomology Laboratory, University of Hawaii at Manoa, on the effects of crystal methamphetamine on the development of another species of sarcophagid fly, *Parasarcophaga ruficornis*. Preliminary results of these studies (unpublished data) show a similar increase in rate of development of maggots when fed on tissues containing crystal methamphetamine, beginning at hour 30 and continuing through hour 60. Unlike the situation observed in heroin, maggots in the control colony attain the greatest size. Pupariation is observed earlier in colonies fed on tissues containing the crystal methamphetamine and the period of pupation is shorter for these colonies. There was an increased mortality observed during the puparial stage for these colonies (up to 60% mortality observed) when compared with the control (9.2% mortality). As noted above, these results are preliminary and further studies are needed.

While there have been, to date, few applications of these data, the case presented by Lord (1991) illustrates the potential significance of these alterations in the rate of larval development. The corpse of a caucasian female, approximately 20 years of age, was discovered in a pine woods area NE of Spokane. The corpse was physically in the early bloat stage of decomposition, with an extensive population of maggots on the face and upper torso. Maggots were submitted after 5 days of refrigeration and reared to the adult stage on beef kidney. There were 2 species present: *Cynomyopsis cadaverina* and *Phaenicia sericata*. *Phaenicia sericata* typically oviposits within 24 hours following death and C. cadaverina oviposits 1 to 2 days following death. There were 3 classes of maggots present based on total length. The first consisted of maggots measuring 6-9 mm in length and consistent with an interval of 7 days. The second consisted of smaller maggots, indicative of multiple broods under development. The third class consisted of a single maggot from the nasopharyngeal area, measuring 17.7 mm in total length and indicating a time

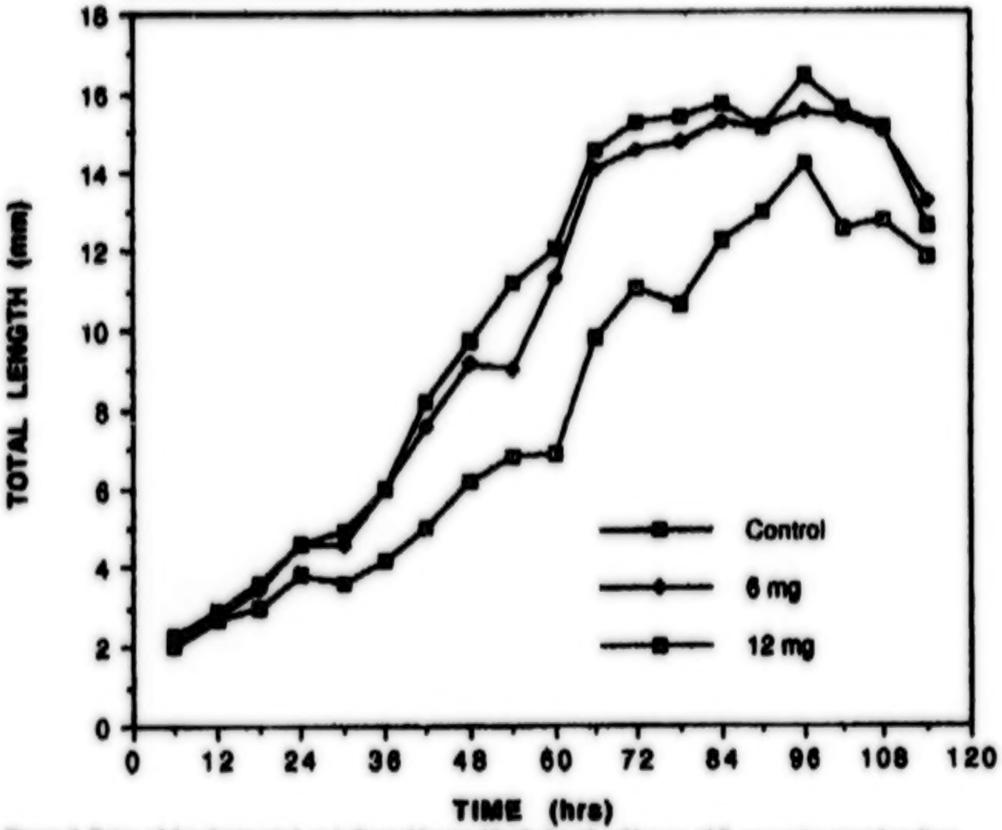

Figure 6. Rates of developmental, as indicated by total body length, of larvae of *B. peregrina* reared on liver tissues from rabbits dosed with 6 and 12 mg of heroin.

period of approximately 3 weeks. This time period was not possible given other data associated with this corpse. The possibility that the maggot had migrated from another nearby source was ruled out, as no such carrion were located by investigators and the probability that more than one maggot of that size would have been found. An alternate explanation was that this maggot's growth had been enhanced in a particular pocket in the nasal region containing a concentration of cocaine. A subsequent investigation showed the victim had a history of cocaine abuse and a witness later testified that the victim had snorted cocaine shortly before her death.

CONCLUSIONS

Insects and other arthropods can prove to be valuable tools in investigations of homicide, suicide, or other unattended deaths. In addition to the recognized applications to estimation of postmortem intervals, insects may serve as reliable alternate specimens for toxicological analyses in the absence of tissues and fluids normally taken for such purposes. In cases of decomposed remains, analyses of insects may give more accurate qualitative analyses than the decomposed tissues. While the data presented above concerning the effects of drugs in tissues on the rate of development of Diptera larvae are limited in scope, it is not unreasonable to assume that other substances in tissues may also produce changes in the rates and/or patterns of development. Until appropriate baseline data are available, care must be taken in interpretations of arthropod developmental patterns in

Table 2. ADULT EMERGENCE, PUPAL DURATION AND TOTAL DEVELOPMENTAL PERIOD FOR COLONIES OF *B. PEREGRINA* REARED ON RABBIT LIVER TISSUE CONTAINING VARYING AMOUNTS OF HEROIN*.

Colony	Total Pupae Obtained	% Emerging	$\bar{X}$ Duration in Hours of Pupal State (Range)	$\bar{X}$ Total Development Period (Range)
Control	451	89	253 (246 -276) a	397 (378-432) b
6 mg	209	95	271 (254-282) b	406 (386-450) b
12 mg	150	88	279 (272-282) c	422 (404-450) c
18 mg	338	97	273 (272-312) bc	411 (404-456) bc
24 mg	310	89	281 (288-194) c	439 (408-450) c

*Figures in a column followed by the same letters are not significantly different ($P>0.05$).

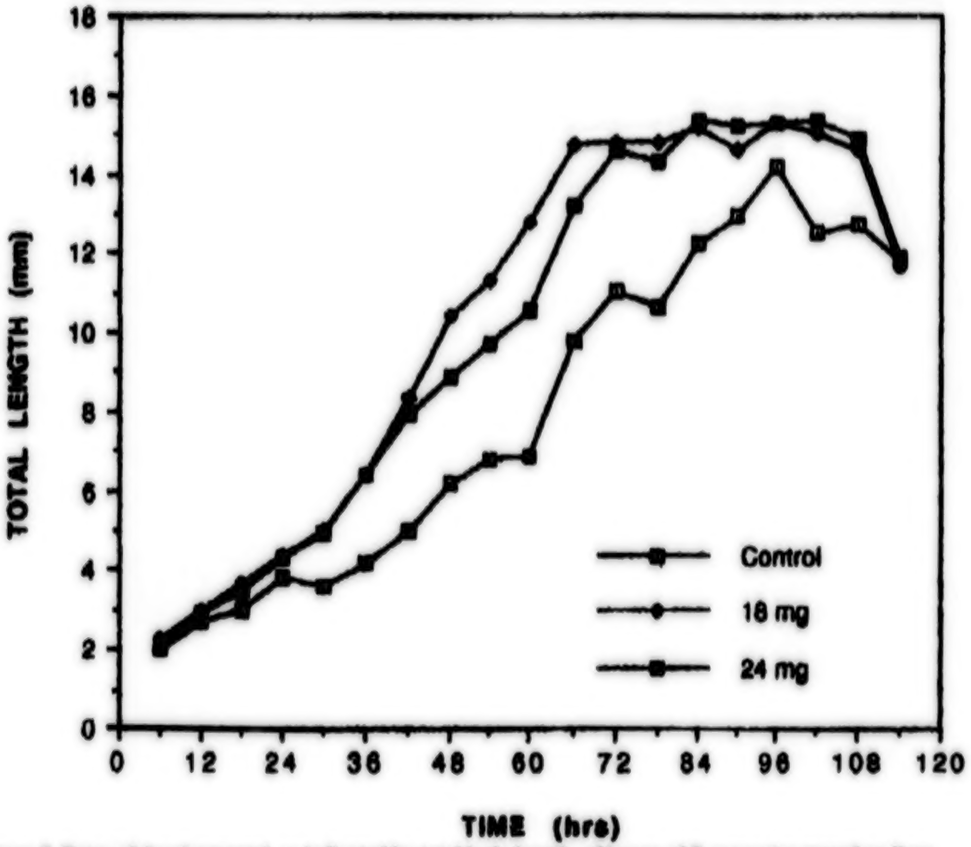

Figure 7. Rates of developmental, as indicated by total body length, of larvae of *B. peregrina* reared on liver tissues from rabbits dosed with 18 and 24 mg of heroin.

cases where drugs or toxins may be a factor. In addition, it becomes essential that the forensic entomologist be made aware of any data indicating the presence of these substances in the remains. This will allow for corrections of the life cycle data, based on the substances involved, and result in more accurate interpretations.

REFERENCES

Baumgartner, W. A., Hill, V. A. and Blahd, W. H. (1989). Hair analysis for drugs of abuse, J. Foren. Sci. 34:1433-53.

Beyer, J. C., Enos, W. F. and Stajic, M. (1980). Drug identification through analysis of maggots, J. Foren. Sci. 25:411-12.

Goff, M. L. (1991). Comparison of insect species associated with decomposing remains recovered inside dwellings and outdoors on the island of Oahu, Hawaii, J. Foren. Sci. 36:748-53.

Goff, M. L., Grown, W. A., Hewadikaram, K. A. and Omori, A. I. (1991). Effects of heroin in decomposing tissues on the development rate of Boettcherisca peregrina (Diptera: Sarcophagidae) and implications of this effect on estimation of postmortem intervals using arthropod developmental patterns, J. Foren. Sci. 36:537-42.

Goff, M. L and Flynn, M. M. (1991). Determination of postmortem interval by arthropod succession: a case study from the Hawaiian Islands, J. Foren. Sci. 36:607-14.

Goff, M. L. and Odom, C. B. (1987). Forensic entomology in the Hawaiian Islands: three case studies, Am. J. Foren. Med. Pathol. 8:45-50.

Goff, M. L., Omori, A. I. and Goodbrod, J. R. (1989). Effect of cocaine in tissues on the development rate of Boettcherisca peregrina (Diptera: Sarcophagidae), J. Med. Entomol. 26:91-93.

Graham, K. G. Koren, Klein, J., Schedderman, J. and Greenwald, M. (1989). Determination of gestational cocaine exposure by hair analysis, J. Am. Med. Assoc. 262:3328-30.

Gunatilake, K. and Goff, M. L. (1989). Detection of organophosphate poisoning in a putrefying body by analyzing arthropod larvae, J. Foren. Sci. 34:714-16.

Introna, F., Jr., LoDico, C., Caplan, Y. H. and Smalek, J. E. (1990). Opiate analysis in cadaveric blow fly larvae as an indicator of narcotic intoxication, J. Foren. Sci. 35:118022.

Kintz, P., Godelar, B., Tracqui, A., Mangin, P., Lugnier, A. A. and Chaumont, A. J. (1990a). Fly larvae: a new toxicological method of investigation in forensic medicine, J. Foren. Sci. 35:204-07.

Kintz, P., Tracqui, A., Ludes, B., Waller, J., Boukhabza, A. Mangin, P., Lugnier, A. A. and Chaumont, A. J. (1990b). Fly larvae and their relevance to forensic toxicology, Am. J. Foren. Med. Pathol. 11:63-65.

Leclercq, M. and Brahy, G. (1990). Entomologie et medecine legale: origines, evolution, actulaisation, Rev. Med. Lieg. 45:348-58.

Lord, W. D. (1991). Case histories of the use of insects. In: Entomology and Death: A Procedural Guide, (Catts, E. P., Jr. and Haskell, N. H., eds.), Joyce's Print Shop, Clemson, S. C. pp. 9-37.

Lord, W. D., Catts, E. P., Scarboro, D. A. and Hadfield, D. B. (1986). The green blow fly, Lucilia illustris (Meigen), as an indicator of human post-mortem interval: a case of homicide from Fort Lewis, Washington, Bull. Soc. Vector Ecol. 11:271-75.

Nuorteva, P. (1977). Sarcosaprophagous insects as forensic indicators. In: Forensic Medicine: A Study in Trauma and Environmental Hazards, (Tedeschi, C. G., Eckert, W. C. and Tedeschi, L. G., eds.), Vol. 2, W. B. Saunders, Toronto, pp. 1072-95.

Nuorteva, P. (1987). Empty puparia of Phormia terraenovae R.-D. (Diptera: Calliphoridae) as forensic indicators, Ann. Entomol. Fenn. 53:53-56.

Nuorteva, P. and Nuorteva, S. L. (1982). The fate of mercury in sarcosaprophagous flies and in insects eating them, Ambio 11:34-37.

Schott, S. and Nuorteva, P. (1983). Metylkvicksilvrets inverkan pa aktivitetet hos Tenebrio molitor (L.) (Col. Tenebrionidae), Acta Entomol. Fenn. 42:78-81. (English summary).

Sohal, R. S. and Lamb, R. E. (1977). Intracellular deposition of metals in the midgut of the adult housefly, Musca domestica, J. Insect Physiol. 23:1349-54.

Sohal, R. S. and Lamb, R. E. (1979). Storage-excretion of metallic cations in the adult housefly, Musca domestica, J. Insect Physiol. 25:119-24.

Utsumi, K. (1958). Studies on arthropods congregating to animal carcasses, with regard to the estimation of postmortem interval, Ochanomizu Med. J. 7:202-23, (english summary).

AUTOMOTIVE PAINT SYSTEMS IDENTIFICATION

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Forensic paint analysis is most often associated with cases of forced entry, burglary, and/or vehicular hit and run. This paper will deal with only automotive paint systems identification associated with hit and run cases. The purpose of forensic paint examinations is to associate evidential material found at a specific location with a source. To adequately accomplish this goal the forensic scientist must overcome a number of problems associated with paint evidence.

First, the paint industry is one of the most chemically complex found in today's society, utilizing as many as 600 different types of raw materials to develop a finished coating product (Thornton 1981). The industry is ever changing with polymer chemists developing new products almost daily for both architectural and vehicular use. The great diversity of chemical components used in paint manufacturing, coupled with the marketing of new and improved coatings technology, challenges one's ability to analyze samples properly and maintain the necessary knowledge to correctly interpret results.

Secondly, the forensic scientist often is requested to compare and/or identify paint samples whose sizes range from 1 mm to less than 100 μ. Analyzing evidence of this size demands a systematic approach which is as non-destructive as possible and as informative as necessary for appropriate identification.

Finally, there exists an inherent problem in paint analysis, the class characteristic nature of paint. With physical evidence and the testimony of expert witnesses playing an increasingly important role in our judicial system, it is the responsibility of forensic scientists not only to report their results, but also to interpret them accurately and with an appropriate degree of significance.

Solutions to these problems can be accomplished only through a multi-system analytical approach. This paper examines several systems used in the author's laboratory, explains the significance each brings to the identification process, and explores the probative meaning of the results obtained from them. In addition, the author presents several techniques and tools useful in sample manipulation, preparation, and identification, and graphically demonstrates the importance of forensic paint analysis through case examples.

VIDEO PRESENTATION

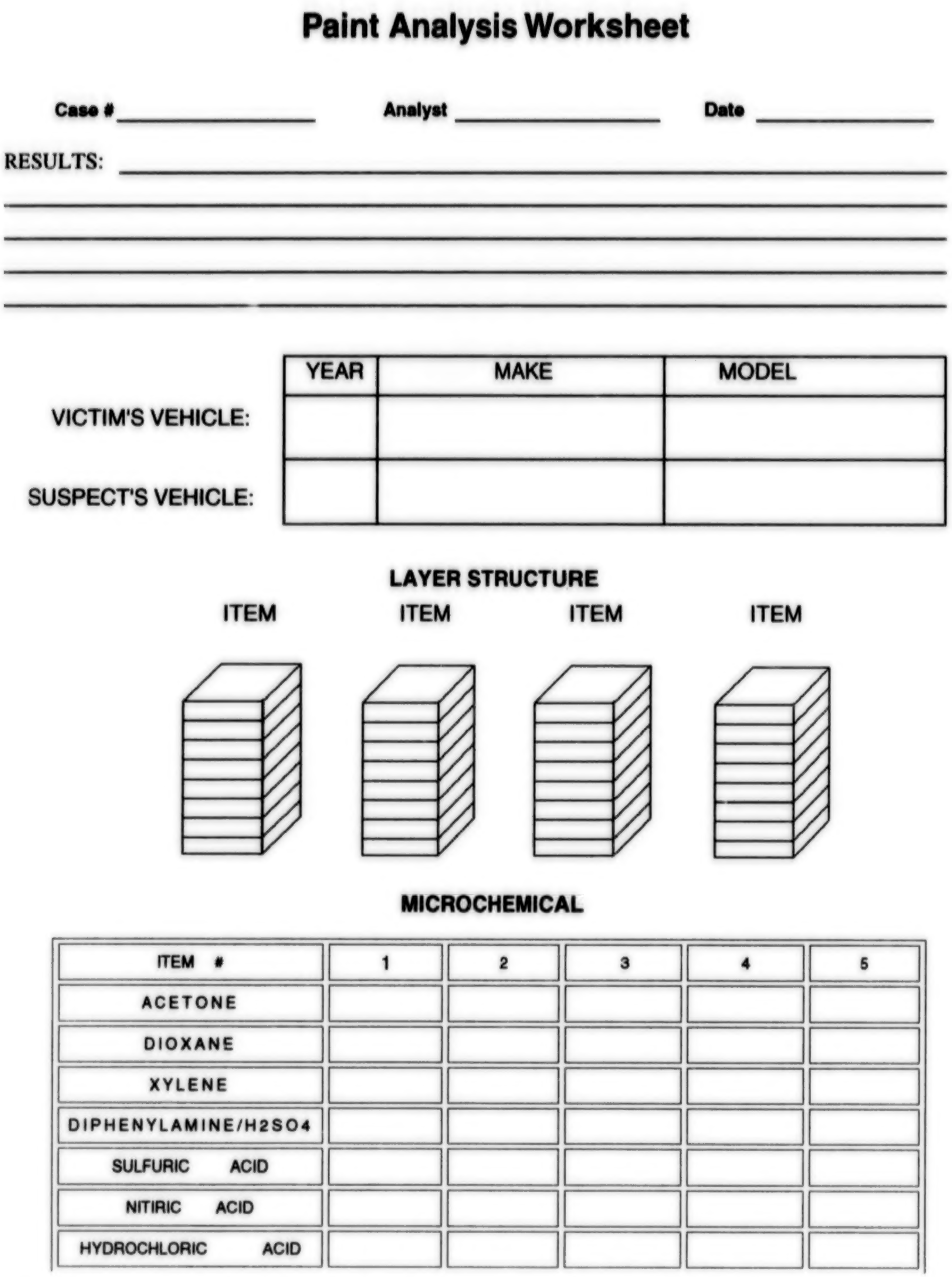
During the symposium a video was presented in which an actual hit and run scene occurred which was taped from the trooper's patrol car. In the early morning hours of February 16, 1991, a Georgia State Patrol Trooper stopped a suspected violator, asked the driver to step out of his vehicle and engaged him in conversation. The following is from a 60 second video tape which showed the events.

> The State Trooper moves to the back of the suspected violator's vehicle, converses with the driver and determines that there is a passenger in the vehicle. The trooper advises the driver to remain at the back of his vehicle and, moving to the driver's side window looks inside the vehicle. At this time the driver moves toward the trooper who turns to him and once again instructs him to stay at the back of the vehicle. The trooper moves to escort the driver to this position and then returns to look inside the driver's side window. At this moment a passing vehicle swerves off the roadway, striking the trooper in the right upper thigh,and slamming him against the suspected violator's vehicle.

As the viewers observed, the hit and run vehicle struck so quickly that it was difficult to determine visually its make, model or color. The video tape clearly demonstrated a need for an appropriate paint analysis system to evaluate physical evidence and make these important determinations. During the course of this paper, as methods of paint analysis used in our laboratory are described, evidence from this case is used to exemplify these descriptions.

EXAMINATION PROCEDURE

In order to begin a systematic forensic paint examination the author has found it prudent to use a paint analysis worksheet. The worksheet (Figure 1) not only aids in leading the analyst through a step by step, logical procedure, but also creates a record of specific results readily available for review while writing a report or preparing for courtroom testimony.



Paint Analysis Worksheet

Case # ______________ **Analyst** ______________ **Date** ______________

RESULTS: ____

	YEAR	MAKE	MODEL
VICTIM'S VEHICLE:			
SUSPECT'S VEHICLE:			

LAYER STRUCTURE

ITEM
ITEM
ITEM
ITEM

MICROCHEMICAL

ITEM #	1	2	3	4	5
ACETONE					
DIOXANE					
XYLENE					
DIPHENYLAMINE/H2SO4					
SULFURIC ACID					
NITIRIC ACID					
HYDROCHLORIC ACID					

Figure 1. Example of forensic paint analysis worksheets (pages 1 and 2) used in the author's laboratory for documenting results obtained during a paint analysis.

Paint Analysis Worksheet Page 2

Case # ________________ **Analyst** ________________ **Date** ________________

INORGANIC

Carbon Stub Map

	Mg	Al	Si	P	K	Ca	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ag	Cd	Sn	Sb	Ba	Pb	Other
ITEM 1																					
ITEM 2																					
ITEM 3																					
ITEM 4																					
ITEM 5																					
ITEM 6																					

ORGANIC

POLYMER TYPE/ITEM	1	2	3	4	5
ACRYLIC LACQUER					
ACRYLIC-ALKYD					
ACRYLIC MELAMINE					
ACRYLIC URETHANE					
ALKYD					
ALKYD MELAMINE					
EPOXY MELAMINE					
EPOXY RESIN					
POLYESTER MELAMINE					
NITROCELLULOSE					
URETHANE MODIFIED ACRYLIC-ALKYD					
UNKNOWN					

DATA BASE LIBRARY SEARCH

	Color Number	Search Value	Match Unknown (Y/N)
Suspect's Vehicle			
Victims's Vehicle			

Figure 1 — Continued. Example of forensic paint analysis worksheets (pages 1 and 2) used in the author's laboratory for documenting results obtained during a paint analysis.

The evidential paint samples are transferred from their submission containers by way of clean white paper funnels into weigh cups which are appropriately labeled. Sample evaluation follows and includes four phases: Microscopic, Microchemical, Inorganic and Organic

MICROSCOPIC

Stereomicroscopic examination is perhaps the most important part of forensic paint analysis. During this examination the scientist observes how much of the questioned material is available, thus determining the course of analysis to follow. The examiner can detect color and layer structure and perform visual color comparisons. Microscopic location of sanding striations on the bottom primer layer and/or identifying more than three layers of paint usually indicates a refinish instead of an original equipment manufacturer (OEM) paint. With a stereomicroscope it is possible to isolate appropriate specimens for further testing even when sample size is quite small.

Layer Structure

A number of techniques can be employed to visualize layer structure microscopically including:

a) angled edge cut
b) on-edge viewing in glycerine
c) individual layer cut down
d) microtoming

These methods are seen in Figure 2. Our laboratory uses the individual layer cut down procedure. A technique for sample manipulation when using this procedure is shown in Figure 3. A sample is placed on a thin smear of Super Glue® on a 75 x 50 mm glass microscope slide and allowed to dry. This allows for optimum sample control by the analyst as he executes a layer by layer dissection and can be performed on samples as small as 50μ. The microanalyst uses a scalpel held at a sharp angle to the sample to peel away thin slices of the paint chip, retaining representative slices from each paint layer for paper insert sample preparation and solubility testing.

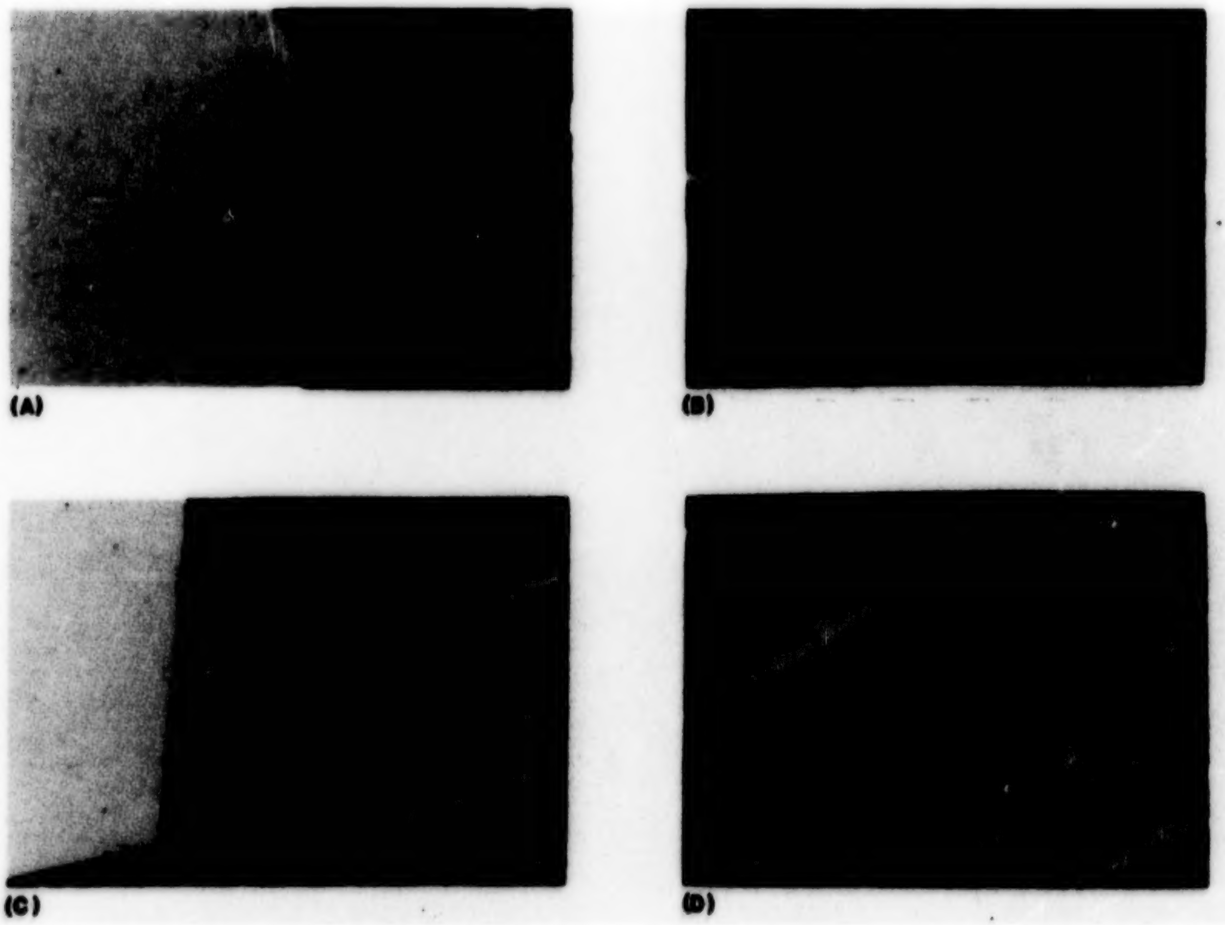


Figure 2. Photographs of four methods for observing layer structure on small paint chips (A) angled edge cut, (B) on edge viewing in glycerine, (C) individual layer cut down, and (D) microtomed cross section.

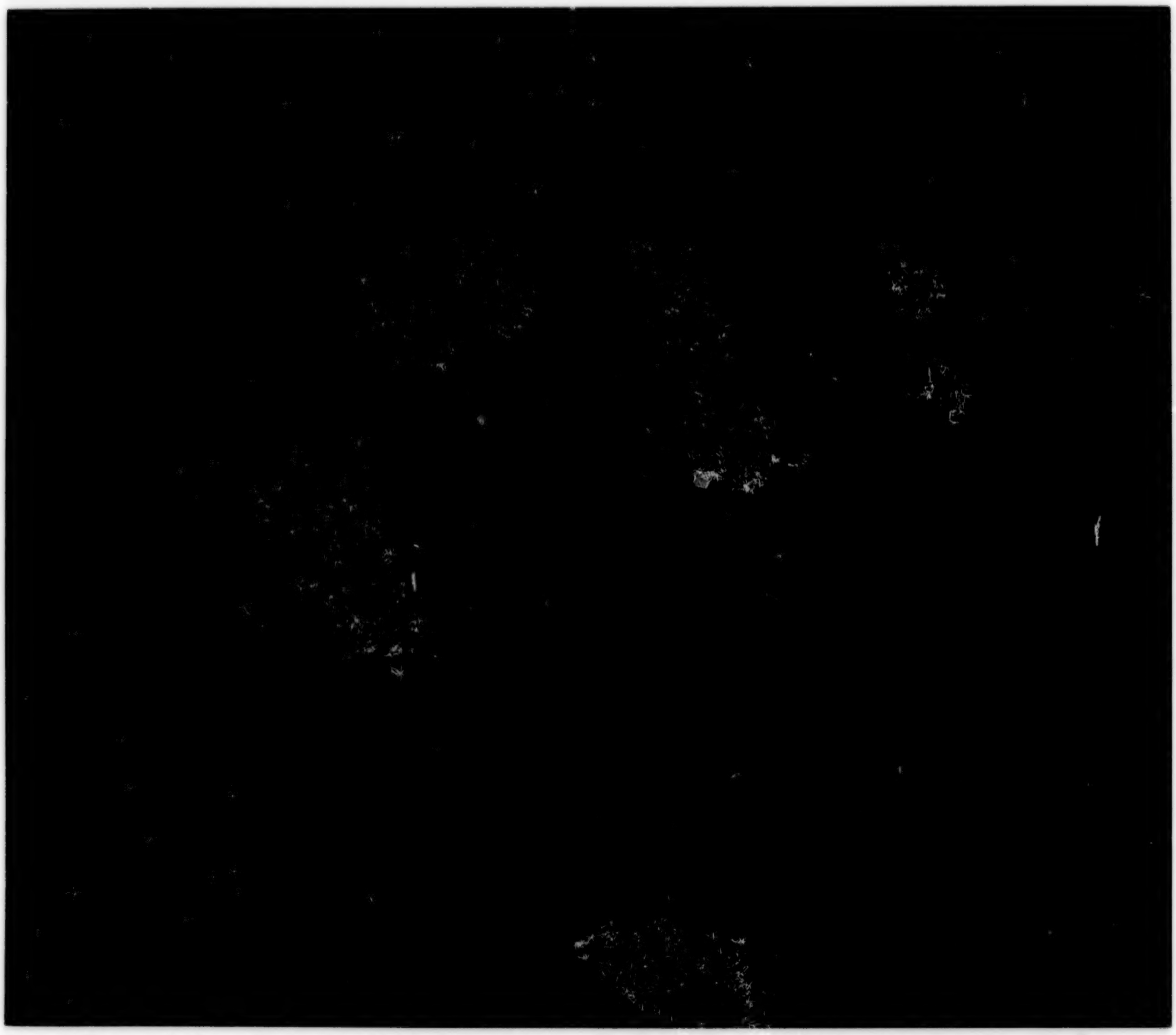


Figure 3. Photograph of a small paint chip which has been attached to a 75 x 50 mm microscope slide by a thin smear of Super Glue®.

Although this sampling technique requires practice, we feel that it has several advantages. The method is rapid, and the analyst can often detect texture characteristics (hardness, etc.) of the individual layers as he cuts through them. Additionally, the slices from each individual paint layer are obtained in a format suitable for further analysis via the sample preparation method described below.

Sample Preparation

Place a thin slice of paint obtained from individual layer cut down on the bare metal area of a 7 mm die press and position in a hand press (Figure 4). Apply moderate pressure to achieve sample flattening and, to a lesser degree, sample thinning. Stereomicroscopically remove the flattened paint via scalpel and/or tweezers and attach one edge to a thin strip of transparent tape

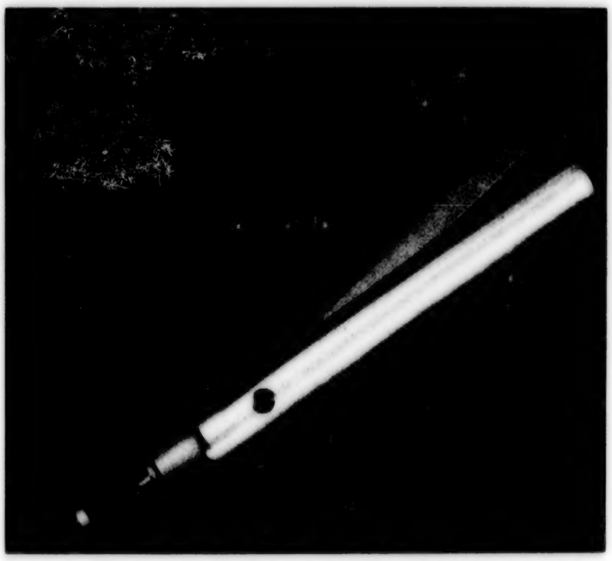


Figure 4. Photograph of a 7 mm metal die and hand press used to flatten paint samples for paper insert preparation.

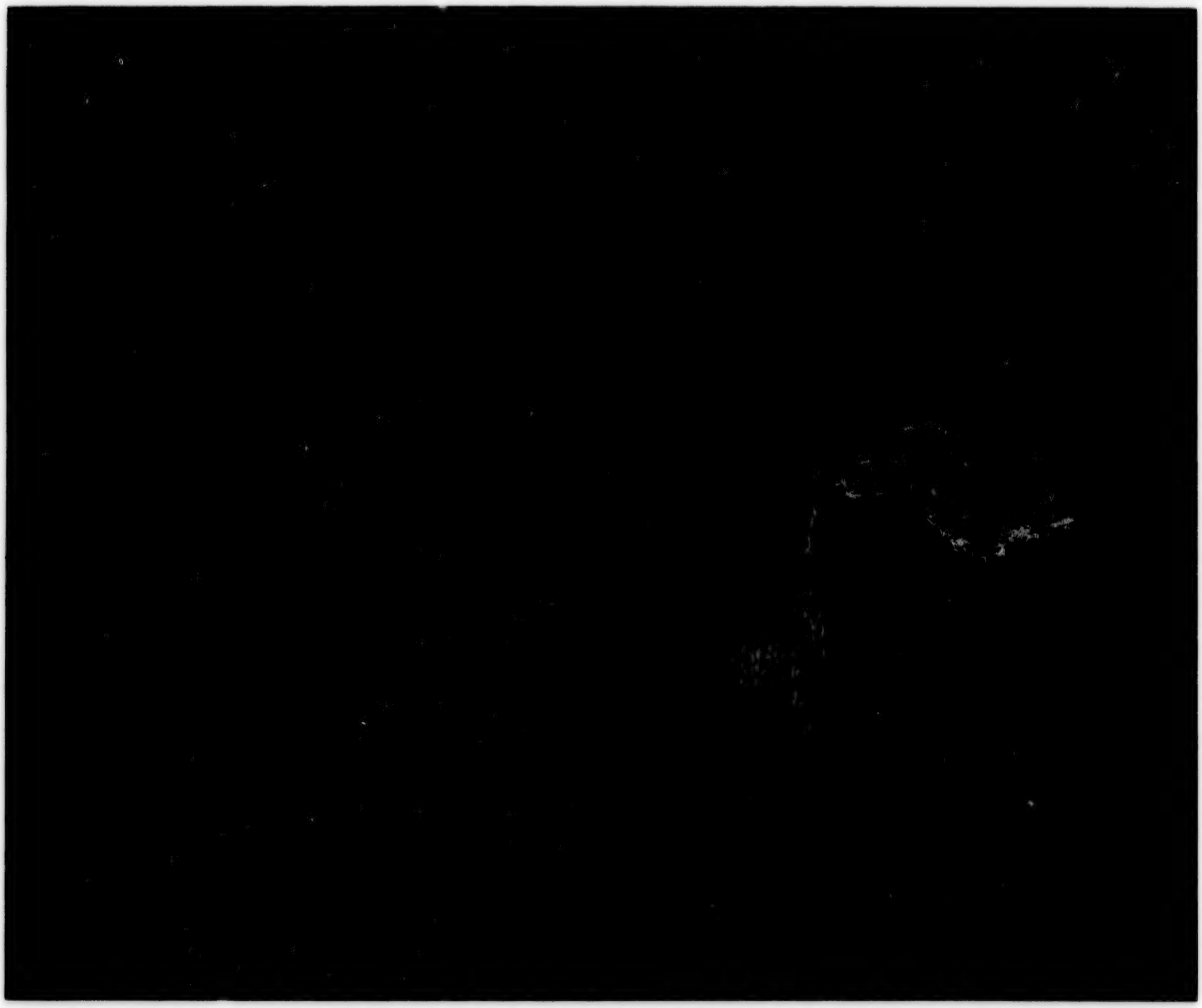


Figure 5. Photograph of a prepared paper insert sample showing the placement of the paint sample relative to the strips of adhesive tape.

which has been laid across the 3 mm aperture of a 13 mm circular paper insert designed for a Spectratech IR Spectroscope sample holder. Place an additional strip of tape across the aperture to attach the free edge of the paint sample, thus creating a paper insert sample (Figure 5).

Paint evidence often takes the form of thinly abraded smears on metal and clothing. An example of this is shown in Figure 6. Here an automotive fender painted with a light blue metallic coating has been struck by a second vehicle leaving thinly abraded darker blue areas. Sample preparation can be accomplished by stereomicroscopically scraping the abraded sample into small mounds (Figure 7) which then can be removed, pressed, and attached to transparent tape as previously described.

Figure 8 shows a barely visible abraded area of paint on the trousers of the State Trooper that was shown in the video. Figure 9 shows a microscopic view of the same area. Sample preparation from this type of evidence often requires a sharp pointed scalpel blade to dissect apart the cloth weave and separate individual fiber strands where minute particles of paint may adhere. With careful and patient dissection a forensic microanalyst can remove samples less than 50 µm in diameter and appropriately prepare them for the paper insert.

A sample thus prepared as a paper insert is now ready for non-destructive, sequential, multi-instrumental evaluation. The techniques used for further characterization are stereomicroscopic and microspectrophotometric color comparisons, transmission microscopic Fourier transform infrared analysis and scanning electron microscopic with energy dispersive x-ray analysis.

Microspectrophotometric Color Comparisons

A number of forensic scientists poignantly attest to the evidentiary value of color in the forensic paint evaluation process (Ryland *et al.* 1981; Laing *et al.* 1980, 1982; Cousins *et al.* 1984 a,b; Nowicki and Patten 1986).

In many instances, however, due to sample size and metameric effects, the forensic analyst must go beyond visual color comparisons and attempt to discriminate paints of similar color by evaluating, wavelength by wavelength through the visible spectrum, absorption, transmission or reflectance of the paint sample. This evaluation is performed in our laboratory with a NanoSpec 10 microspectrophotometer attached to an Olympus BHS microscope with a 100 watt tungsten light source. The prepared paper inserts are taped to the edge of a microscope slide (Figure 10). The slide is placed on the microscope stage in an appropriate position for focusing on the paint sample. At least two areas of the same sample are then scanned from 400 nm to 700 nm.

Figure 11 shows two red paints which are rather easily distinguished when viewed with tungsten lighting. When viewing small samples of these same two paints under florescent lighting, one finds the color discrimination much more difficult. Figure 12A shows transmission curves of the two red paint samples. There are observable differences in the slopes at approximately 600 nm and in the transmission minima (568 nm vs. 576 nm). These quantitative distinctions therefore aid the analyst in eliminating incorrect color interpretation due to metamerism. Figure 12B shows the similarity of the transmission curves of the questioned paint from the trooper's clothing and the known paint from the suspect's vehicle.

MICROCHEMICAL

Upon completion of the visual microscopic examination of submitted paint samples, the analyst is aware of the quantity of both known and questioned samples

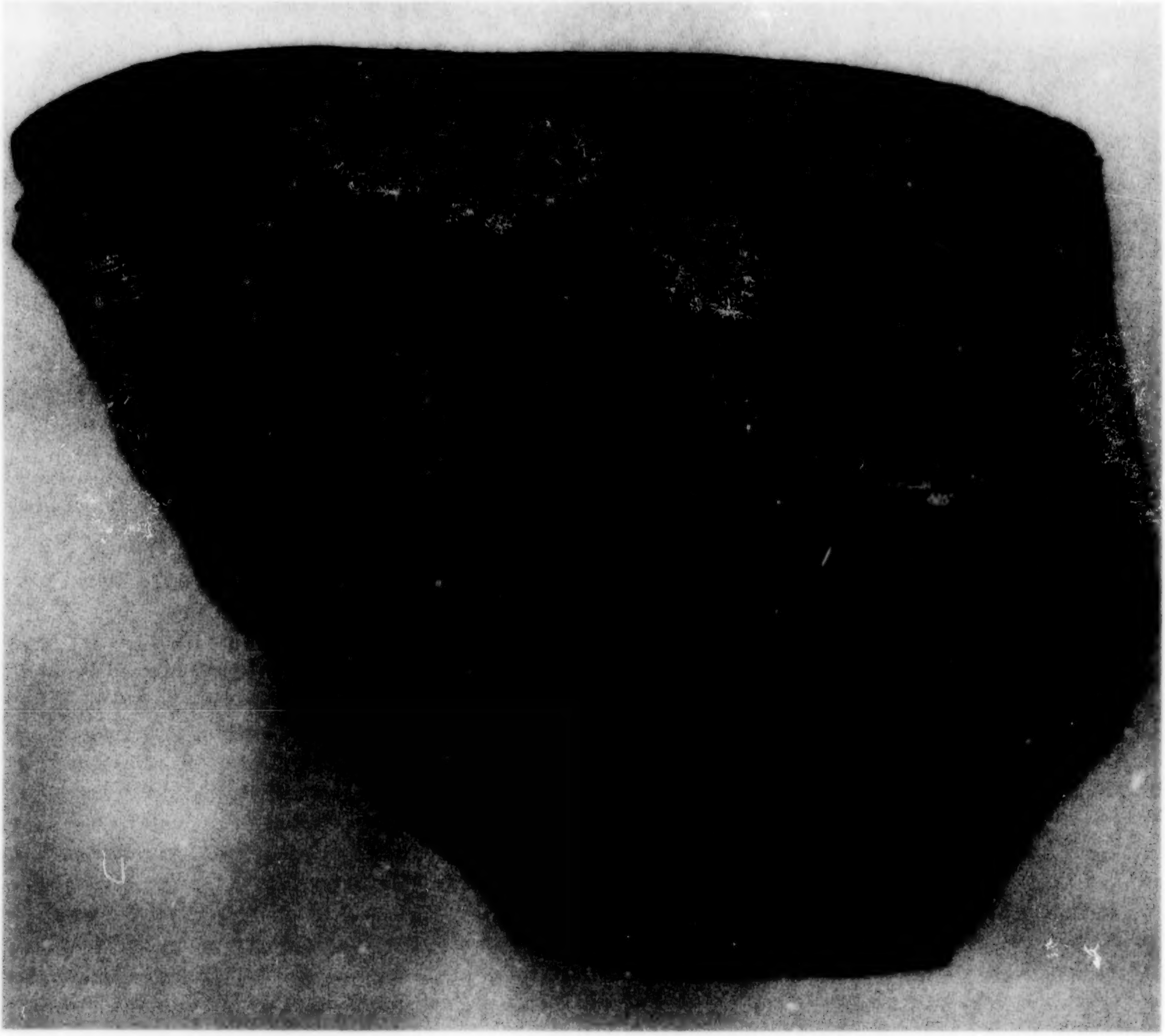


Figure 6. Photograph of a thinly abraded dark blue paint on portion of fender from victim's vehicle.

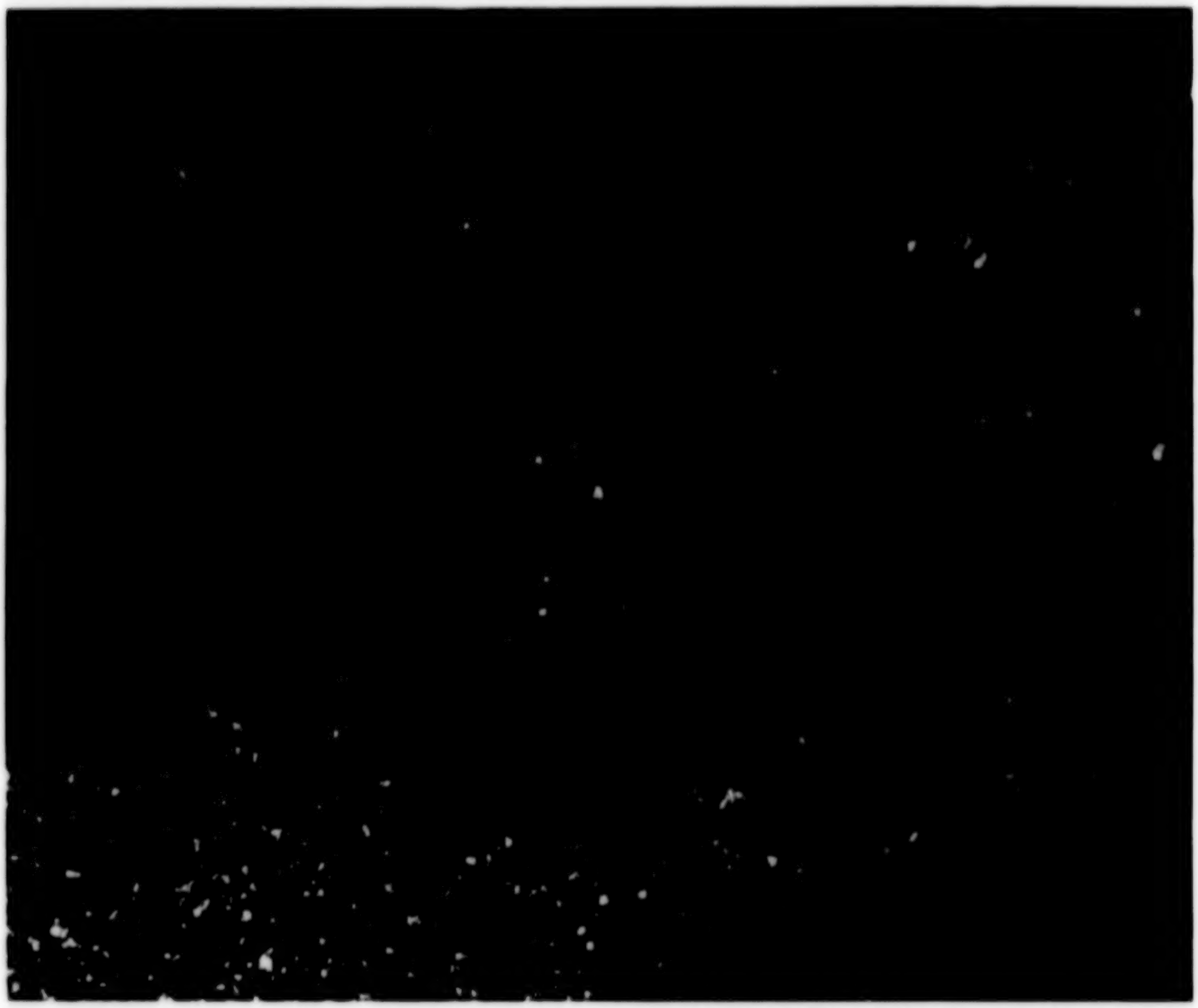


Figure 7. Photomicrograph of questioned paint scraped from dark blue areas shown in Figure 6. This technique allows the analyst to prepare a sample for analysis which contains only questioned paint. The mounds of paint shown in this figure can now be pressed and prepared as a paper insert for instrumental analyses.

available for further testing. Even when the amount of questioned sample is limited, it is important to proceed with the solubility characterization of the known sample(s). These results can assist in determining which reagent systems will provide optimum information when questioned material is limited. Thornton *et al.* (1983) and Castle (1982) have reported a number of reagent systems which can be used to gather binder and pigment compositional information.

SOLUBILITY CHARACTERIZATION

To perform solubility characterization, place samples in the wells of white porcelain spot plates. Add several drops of the reagents listed in Table 1 and observe the sample/reagent mixture microscopically for two to five minutes, and record results and observations on the paint worksheet.

RESULTS AND SIGNIFICANCE OF SOLUBILITY CHARACTERIZATION

Table 1 shows the reagents used and interpretations of possible results from solubility analysis. It is important to note that, using dioxane and xylene, one usually can discriminate rapidly between acrylic solution and acrylic dispersion lacquers. The identification of an acrylic dispersion lacquer indicates an OEM finish. When observing the positive results of a multi-layered paint sample in the diphenylamine/H_2SO_4 reagent, take care in determining which layer elicits the intense blue color. A positive reaction with the top coat of an automotive paint sample is indicative of a refinish paint. The various color changes observed in reactions with concentrated nitric and sulfuric acids are well documented by Castle (1982). His work demonstrates a rapid microchemical method for identifying major pigment groups. Table 2

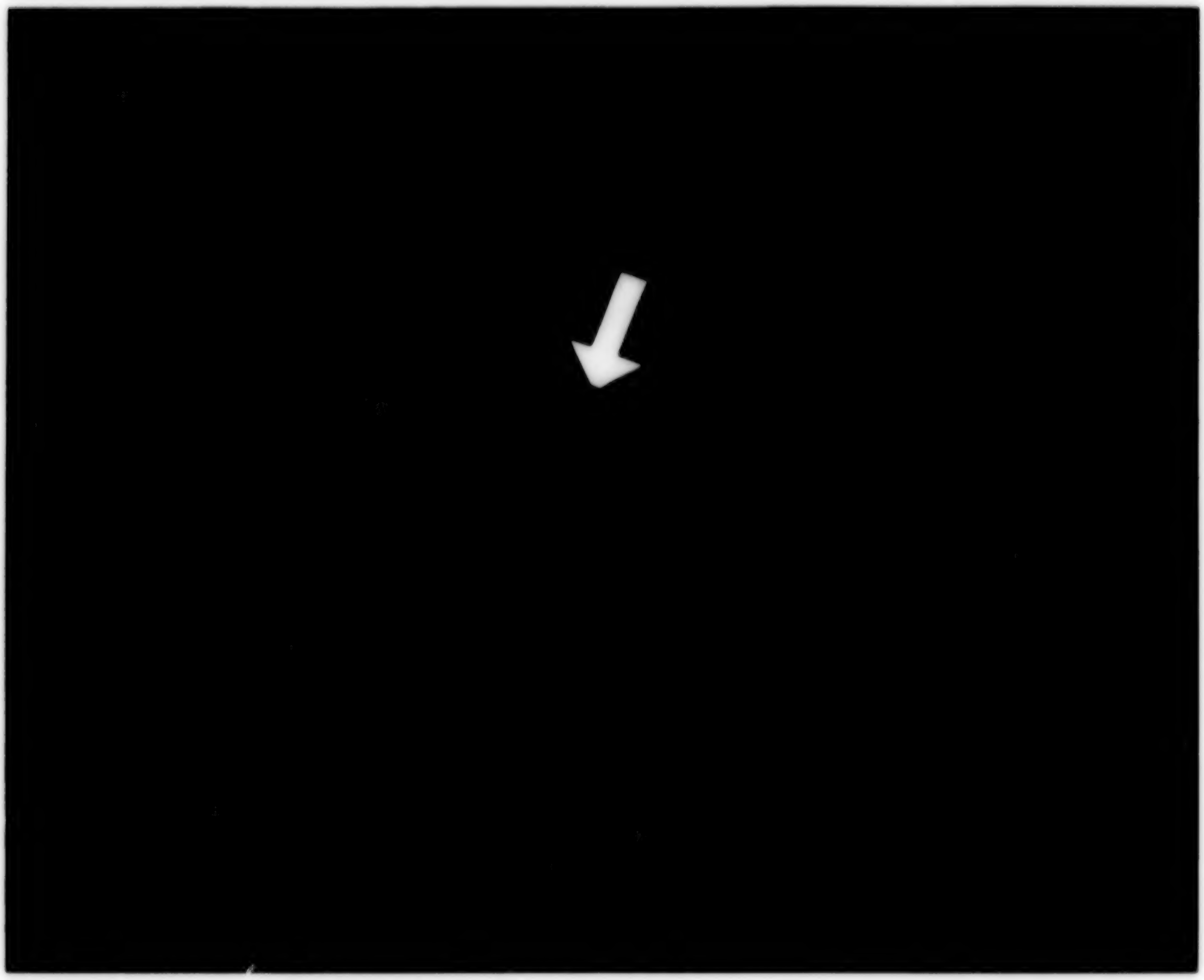


Figure 8. Photograph of an area of abraded paint found on the trooper's pants in the case example.

Table 1. SOLUBILITY CHARACTERIZATIONS AND THEIR SIGNIFICANCE

REAGENT	RESULT	SIGNIFICANCE
Acetone	Soluble	Indicates lacquer binder
	Insoluble	Indicates enamel binder
Dioxane	Soluble	Indicates acrylic solution lacquer or acrylic dispersion lacquer
	Insoluble	Indicates enamel binder
Xylene	Soluble	Indicates acrylic dispersion lacquer
	Insoluble	Indicates acrylic solution lacquer or enamel binder
Diphenylamine/ H_2SO_4	Intense blue bleed	Indicates the presence of nitrocellulose
	No reaction	Indicates the absence of - NO_3 groups
conc. HNO_3 and conc. H_2SO_4	Various color changes	See Castle (1982) for various pigments elucidated using these two acids

Table 2. RESULTS OF SOLUBILITY TESTING OF QUESTION VS. KNOWN

	Questioned Paint from Victim's clothing	Known Paint from Suspect's vehicle
REAGENTS	RESULTS	RESULTS
Dioxane	Soluble	Soluble
Xylene	Soluble	Soluble
Diphenylamine/H_2SO_4	Negative	Negative
Sulfuric Acid	Negative	Negative
Nitric Acid	Negative	Negative

Binder Type Indicated — Acrylic Solution Lacquer

Pigment Type Indicated — None

Figure 9. Photomicrograph of the area of Figure 8 showing the abraded metallic paint bound within the weave of the pants (40X).

shows the results of the solubility tests on the case example involving the trooper.

INORGANIC

Inorganic elemental analysis is necessary for characterization of physical evidence in forensic laboratories (Reeve *et al.* 1976). Paint evidence is no exception. A number of instrumental methods have been used for inorganic elemental analysis including emission spectroscopy, atomic absorption and x-ray diffraction spectrometry and scanning electron microscopy combined with energy dispersive x-ray spectroscopy (SEM/EDX). The former three methods possess disadvantages in difficulty of sample preparation, sample size constraints, time of analysis, and sample destruction (or combination of these). The latter method avoids these drawbacks and avails the analyst with the bonus of morphological and topographical evaluation. The technologically advanced computer/software packages associated with SEM/EDX systems also provide the analyst with innovative data processing for enhanced interpretation and evaluation. Because of these advantages, this technique is the method of choice in our laboratory.

Several methods of sample preparation are used by our laboratory for SEM/EDX analysis of paint samples. All samples are evaluated on 14 mm carbon stubs which have been covered with double-sided sticky tape. If only top coat analysis is required and sample availability is limited, the previously described paper insert sample can be mounted on the carbon stub and analyzed. If sample quantities are sufficient and multi-layer analysis is required, multiple samples can be placed on edge around the periphery of the stub. The positions and descriptions of the samples are mapped on the paint worksheet as shown in Figure 1. Finally, a more time intensive technique involves embedding the sample in mounting media, microtoming and polishing it. This latter technique provides excellent layer structure imaging and the smooth, flat surfaces required for accurate semi-quantitative analysis. With each of these methods, the samples are placed in a vacuum evaporator and coated with a thin layer of carbon prior to placement in the SEM.

The instruments used in our laboratory consist of a Cambridge Stereoscan 200 SEM interfaced with a Tracor Northern 5500 energy dispersive x-ray analyzer and programmable automated stage controller. Samples are analyzed at an operating voltage of 25 keV, 25 mm working distance, 35 degree take off angle, backscattered imaging mode and variable magnifications depending on sample size.

Backscattered detectors in the SEM produce images of high energy electrons which have been produced by beam electron/sample atomic nuclei collisions. These collisions result in path reversal of the electrons, and those with sufficient energy to reach the sample surface are detected. Figure 13 shows a backscattered image of a multi-layer paint which has been prepared by the embedding and polishing technique. The use of backscattered detectors for imaging in scanning electron microscopes affords the user with the advantage of sample topogra-

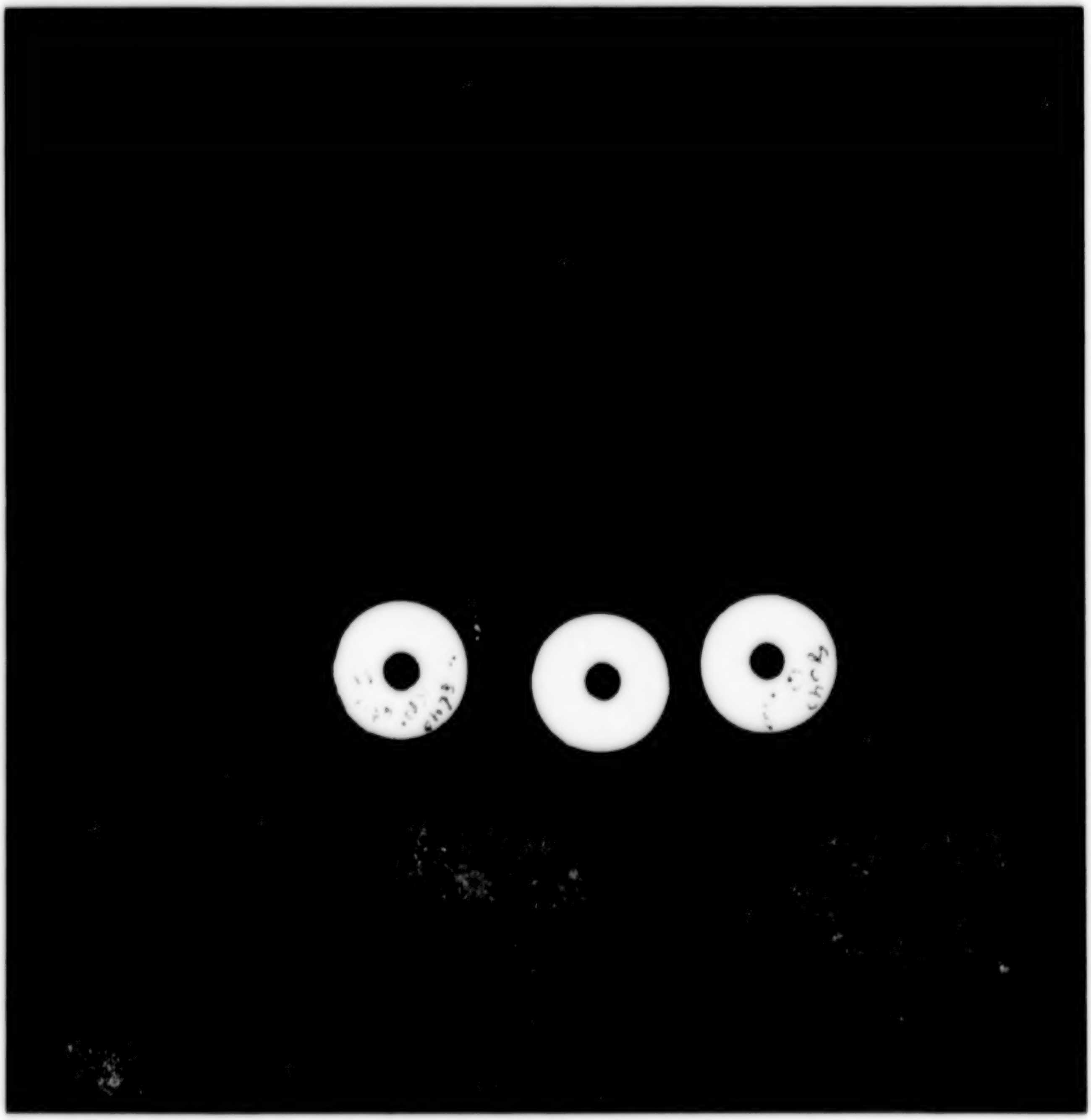


Figure 10. Photograph of prepared paper insert samples attached to 50 x 75 mm microscope slide.

Figure 11. Photomicrograph of two red paint samples (Collaborative Testing Service, CTS BN80 0628 and CTS BC82 0912) viewed under tungsten lighting.

phy and atomic number discrimination. The lighter shaded layers in Figure 13 are those layers containing elements with higher atomic number (Z). Figure 14 shows the associated EDX spectra obtained from the first four layers of the sample. Notice the presence of lead (Z=89) in layers one and three, which correspond to the lighter shaded layers shown in Figure 13.

As noted previously, the computer and software capabilities of EDX systems have added new dimensions in analyzing and viewing data. Figure 15 shows an elemental line scan and associated image of the previously described paint sample. The horizontal red trace line on the right side of this figure indicates the area over which the analysis was performed. The small vertical red cursor line corresponds to the large vertical red cursor line in the segmented line scan on the left side. In this figure, the line scan indicates the presence of titanium and silicon in layer three of the paint sample.

Another computer processing technique which can be valuable in interpretation is elemental composite displays. Software processing allows for the overlapping of x-ray map images and video images. This process is shown in Figure 16A. In this figure the backscattered video image of the sample is shown beside the associated color composite display of the sample. The legend in Figure 16B shows the software assigned element color representation for the composite display. The backscattered image suggests the presence of eight layers, however close examination of the composite display reveals layer 5 in the backscattered image to actually contain a titanium/chromium rich layer (5) and a silicon rich layer (6).

Significance of Inorganic Analysis

The inorganic elemental composition of paint can often be related to the types of pigments and extenders

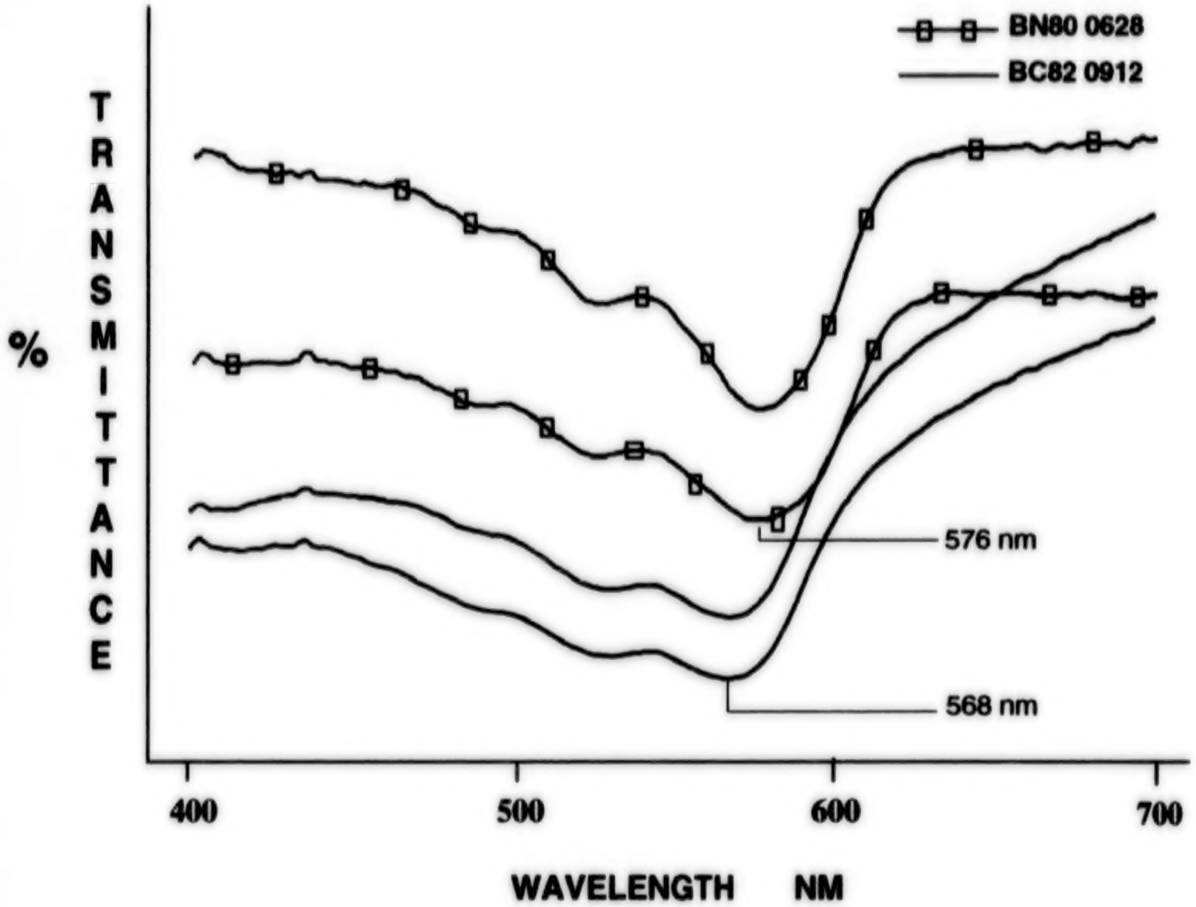


Figure 12. (A) Microspectrophotometric transmission curves of the red paint panels shown in Figure 11. (B) Comparison of the transmission curves of the questioned paint from the trooper's pants and known paint from the suspect's vehicle.

present in the sample. The work of Crown (1968) presents an extensive list of inorganic pigments along with their chemical composition and the coating color in which they are used. Comparing this list with the color and elemental analysis results of an unknown sample, the analyst can often determine a probable pigment(s) identification. For example, finding chromium and lead on elemental analysis would suggest the presence of chrome red pigment ($PbCrO_4 \cdot Pb(OH)_2$). Qualitative elemental analysis can also rapidly discriminate paint samples of similar color and organic matrix (Figure 17). The EDX spectra shown in Figure 18 represents the questioned blue metallic paint removed from the trousers shown in Figures 9 and 10 and known paint samples removed from the suspect's vehicle. The spectra indicate matching elemental compositions. As has been shown, inorganic elemental analysis furthers the individualization of paint evidence and is mandatory for a complete characterization in any paint systems identification process.

ORGANIC

A number of instrumental techniques are available for organic component analysis of paint samples, including pyrolysis gas chromatography, infrared microscopy, pyrolysis mass spectrometry, and differential thermal analysis. This presentation will concentrate on microscopic infrared spectroscopy.

Microscopic Fourier Transform Infrared Spectroscopy

As stated earlier, criminalists are constantly faced with the issue of inadequate sample size in attempting to compare and identify evidentiary material. Two recent weapons which have been added to the scientist's arsenal for attacking this problem are Fourier transform infrared (FTIR) spectroscopy systems and the interfaced microscope attachment. These instruments provide the

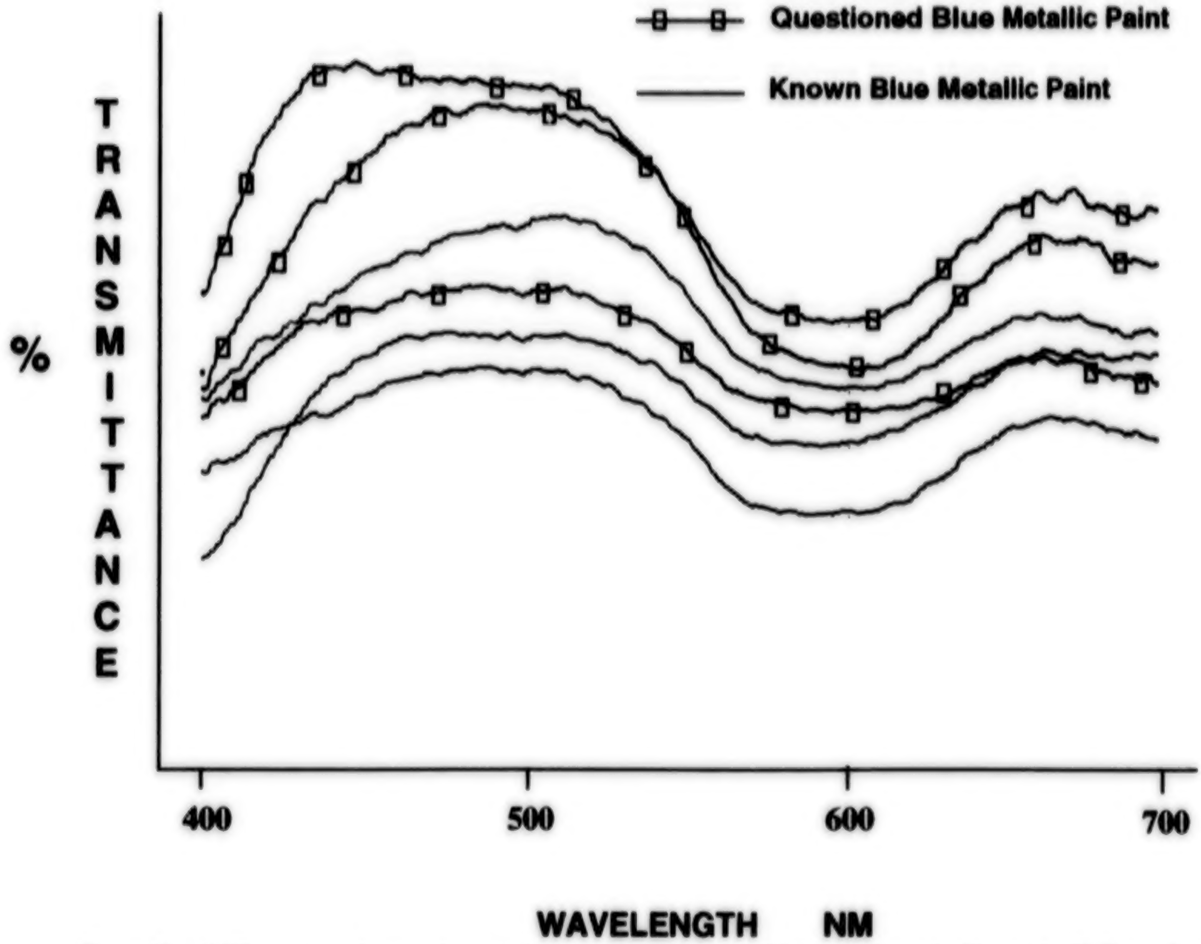


Figure 12. (A) Microspectrophotometric transmission curves of the red paint panels shown in Figure 11. (B) Comparison of the transmission curves of the questioned paint from the trooper's pants and known paint from the suspect's vehicle.

capability of analyzing extremely small paint samples non-destructively.

Transmission samples are prepared for spectral acquisition via the paper insert method previously described (Figure 5). The instrument conditions used in our paint sample analyses are as follows:

Spectrometer: Nicolet Instruments, Madison, WI - 20SXB
Microscope: Spectra-Tech, Inc., Stamford, CT - Spectroscope.
Detector: Mercury Cadmium Telluride (MCT), wide band.
Range: 4000 - 450 CM^{-1}
Resolution: 2 CM^{-1}
Gain: 8
Apodization: Happ-Ganzel.
Area Apertured: Approximately 100 X 100 μm

Using these conditions, excellent spectra can be obtained for interpretation, even from extremely small samples.

Major Automotive Binder Types and Their Classification

In order to continue the process of complete characterization of paint evidence it is necessary to identify the organic matrix or binder in evidentiary paint samples. Numerous workers (Rogers *et al.* 1976a,b; Percy and Audette 1980) have demonstrated the importance of infrared spectroscopy to this identification process. Figure 19 shows the major infrared group frequency regions for paint binder classification. Analyzing infrared spectra for peaks in these regions can rapidly inform the forensic analyst of a class of binder. Table 3 shows the major automotive organic binder types encountered in forensic paint analysis and their usage. Although not indicated in the table be aware that acrylics and acrylic - alkyds can also be urethane modified.

Spectral Interpretation

A general spectral interpretation procedure for binder classification may be initiated as follows (Ryland, personal communication):

1 — Look for melamine (1550 cm^{-1} and 815 cm^{-1}) or urea (1650 cm^{-1}, 770 cm^{-1}) crosslinking.
2 — Look for major bands in the 1300 cm^{-1} to 1000 cm^{-1} range indicative of:

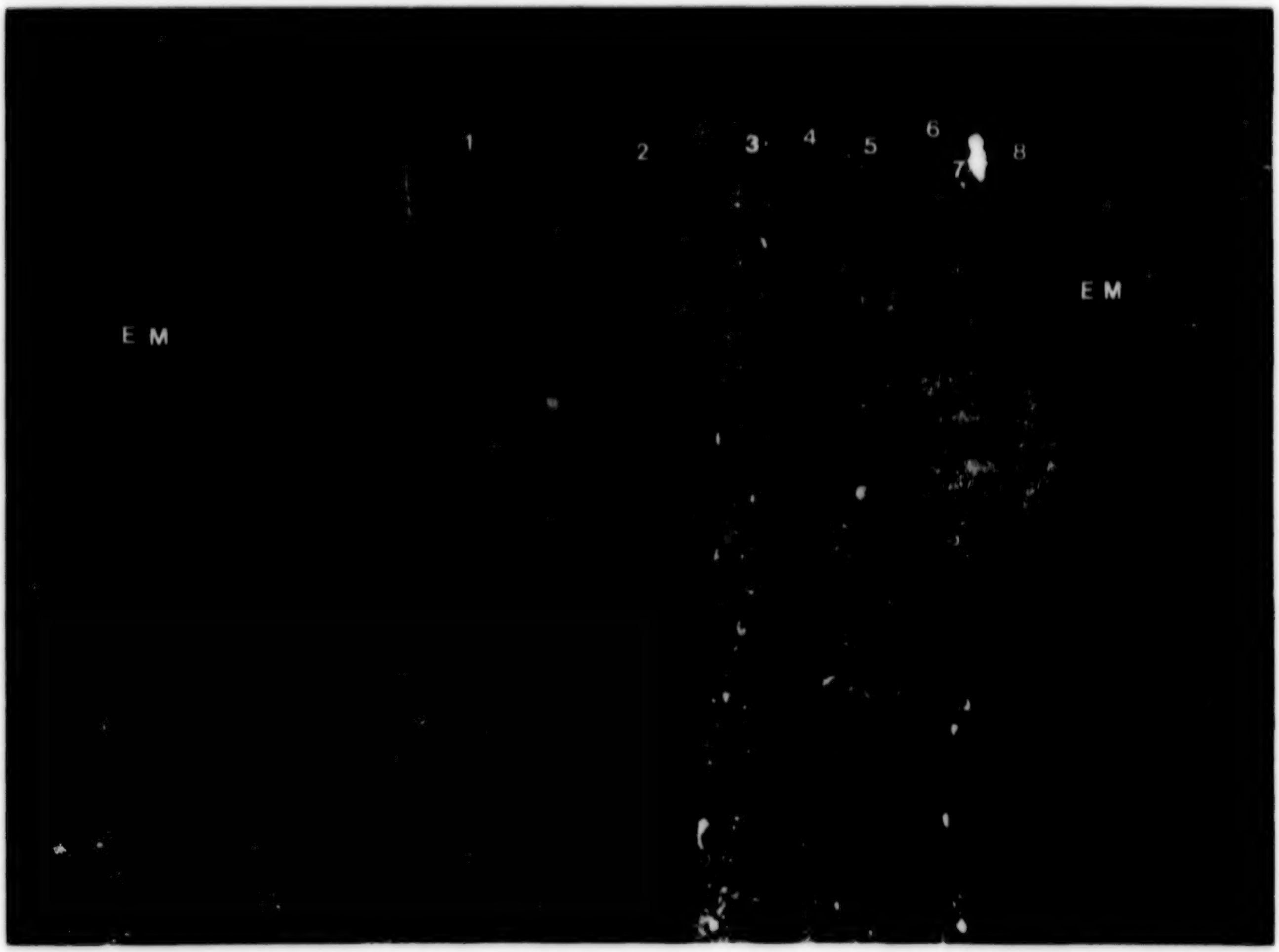


Figure 13. Backscattered scanning electron photomicrograph of the cross section of a multi-layered paint sample. The lighter shaded layers are indicative of elements having higher atomic number (EM = embedding media).

Acrylic - 1150 cm^{-1} to 1170 cm^{-1}
Alkyd - 1260 cm^{-1} to 1270 cm^{-1}
Polyester - 1235 cm^{-1} to 1240 cm^{1}.

3 — Look for urethane (1530 cm^{-1} and absence of 815/830 cm^{-1}) modification.

4 — Look for epoxy (1510 cm^{-1} to 1520 cm^{-1} and 830 cm^{-1}) crosslinking.

Table 3. AUTOMOTIVE PAINT BINDER TYPES CLASSIFIABLE BY INFRARED MICROSPECTROSCOPY

TYPE	USAGE
Acrylic Lacquers	OEM and Refinish
Acrylic - Alkyd Enamels	Refinish
Acrylic Melamine Enamels	OEM
Acrylic - Urethane Enamels	Refinish
Alkyd Enamels	Refinish
Alkyd - Melamine Enamels	OEM and Foreign
Nitrocellulose Lacquers	Refinish
Oxithane Enamels	Refinish
Polyester Enamels	OEM (Ford) and Foreign

This excellent method of classification can lead an experienced spectroscopist to rapid and accurate identification of binder types. To assist those with less experience in infrared spectral interpretation, an automotive paint binder infrared classification flow chart (Figure 20) is presented which systematically allows the interpreter to make yes/no decisions based on both the presence or absence and the intensity of certain spectral peaks, eventually arriving at an identification of one of eleven binder types. Figure 21 A,B,C, and D shows the infrared absorbance spectra of four binder types with their significant peaks labeled. Following these through the flow chart one can see the ease of interpreting complex paint polymer spectra quickly and correctly.

Figure 22 A and B shows the spectra obtained from the case example (clothing and suspect's vehicle). Interpretation of these spectra indicate the paint binders are acrylic lacquers.

Infrared Spectral Data Bases

Most FTIR manufacturers offer a wide range of commercially available spectral data base libraries. These

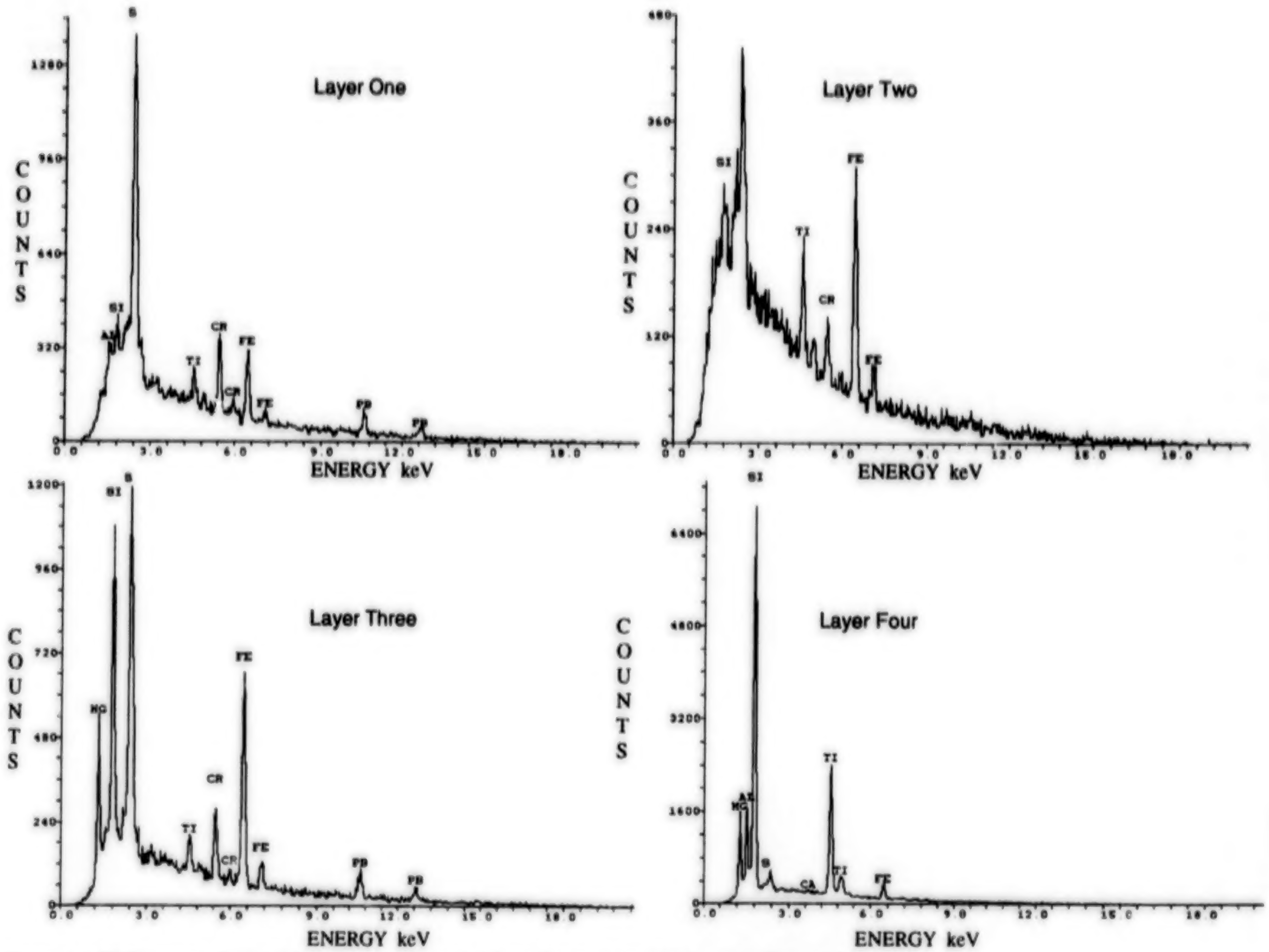


Figure 14. EDX spectra obtained from layers 1 through 4 from the paint sample shown in Figure 13.

tools can be of great assistance to the user when attempting to identify unknown materials. In 1987 the author began the development of an U. S. automotive paint FTIR spectral library. The known automotive paint samples used in development of this library were obtained from Collaborative Testing Services, Herndon, Virginia, and covered the years 1975 - 1989. The library presently contains approximately 2900 spectra which were collected as transmission spectra using the paper insert sampling method and instrument conditions described previously. A preliminary evaluation of this library (Tillman and Bartick 1990) has shown that 9 out of 10 test resamples were first hits. When spectra of questioned paint samples from salvage yard vehicles were searched in a pre-filtered query mode using the absolute derivative search algorithm, the results fell within the top eight spectral hits (Table 4). This limits to a reasonable quantity the number of paint reference panels which need to be compared visually with the questioned paint chips and decreases the time needed for determination of vehicles on which the questioned paint has been used. Table 5 shows the results of searching the spectrum of the questioned paint from the troopers clothing (Figure 22 B) against the GBI - Automotive Paint Chip Library. This figure also provides an accompanying explanation of the results reported by the Nicolet search routine. After obtaining the search results, the color code num-

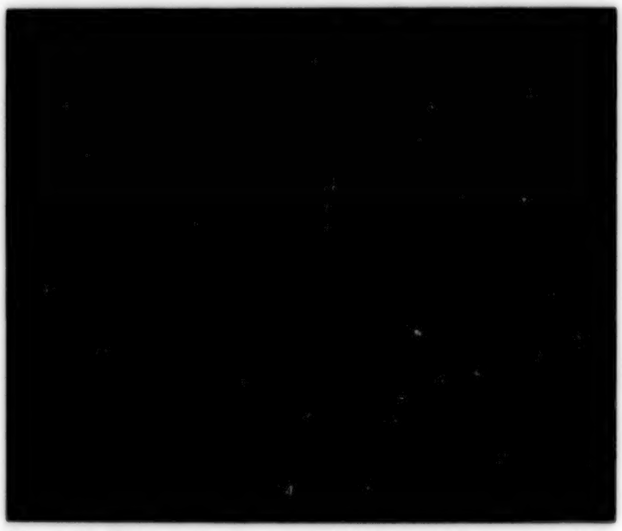


Figure 15. Photograph of a segmented elemental line scan and the associated backscattered image of the multi-layered paint sample.

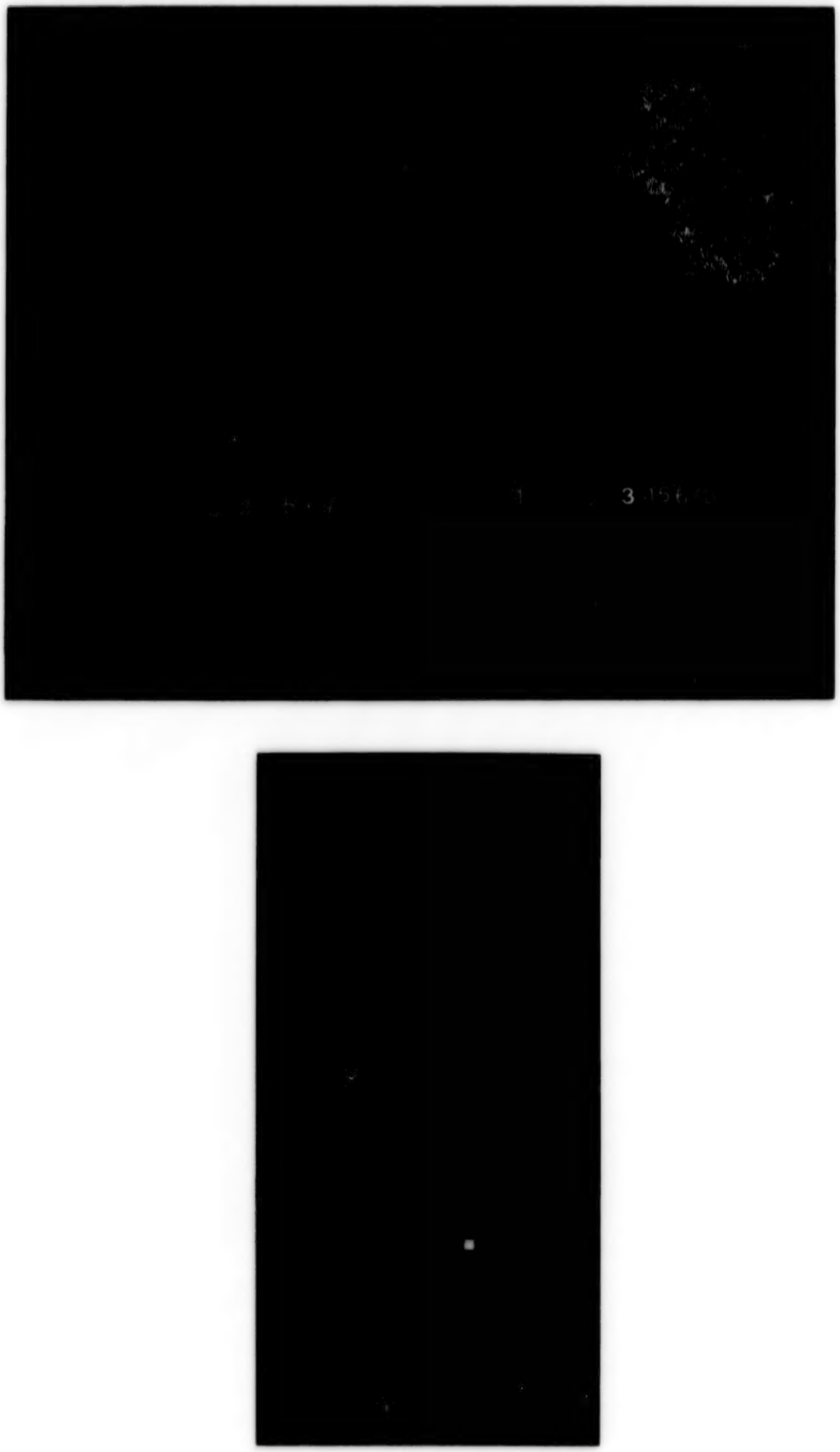


Figure 16. (A) Photograph of a backscattered image of the cross-section of a multi-layered paint sample and its associated computer generated elemental compositional overlay. (B) Photograph of the software assigned element color representation for the composite display.

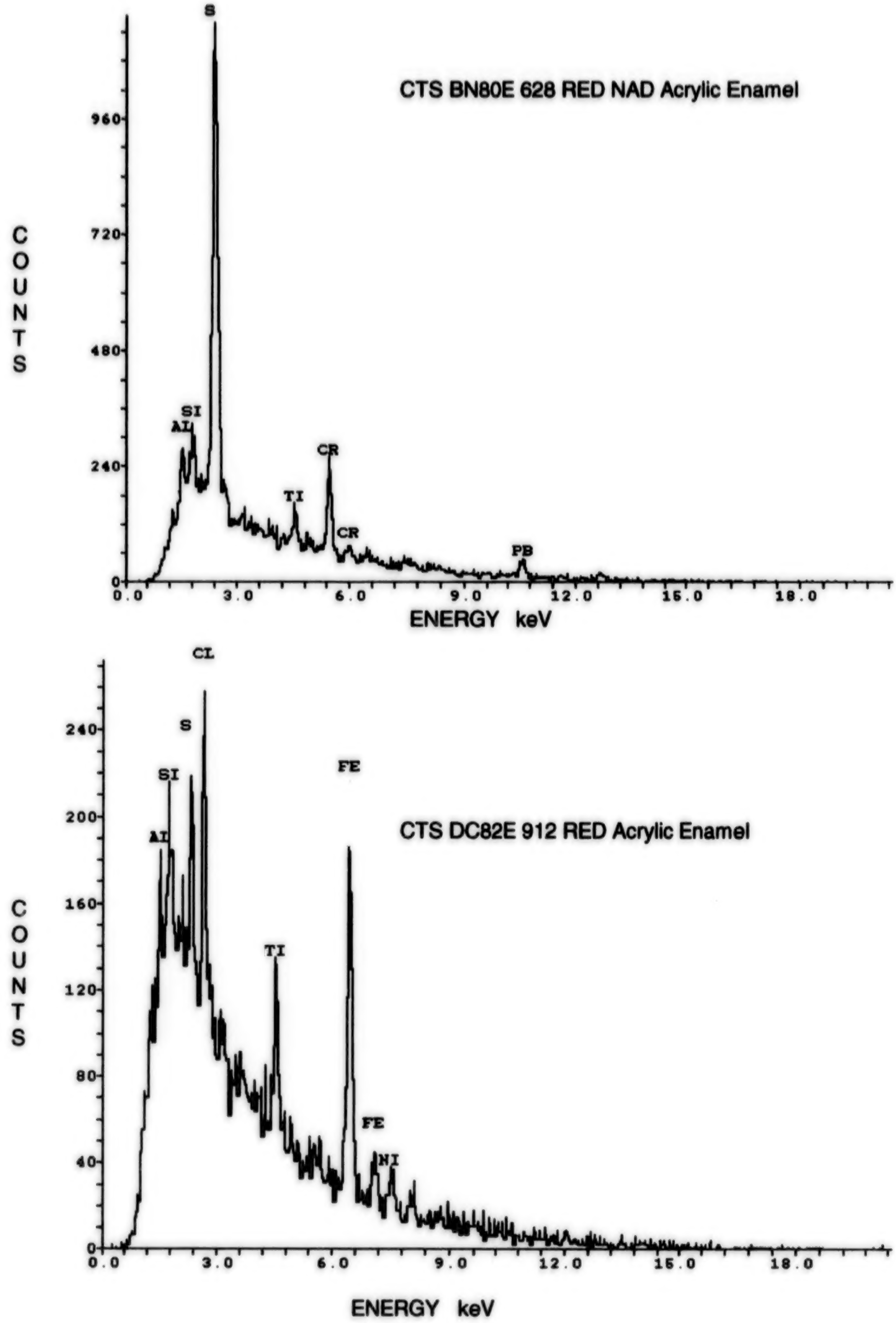


Figure 17. EDX spectra of the two red acrylic enamel paint samples shown in Figure 11.

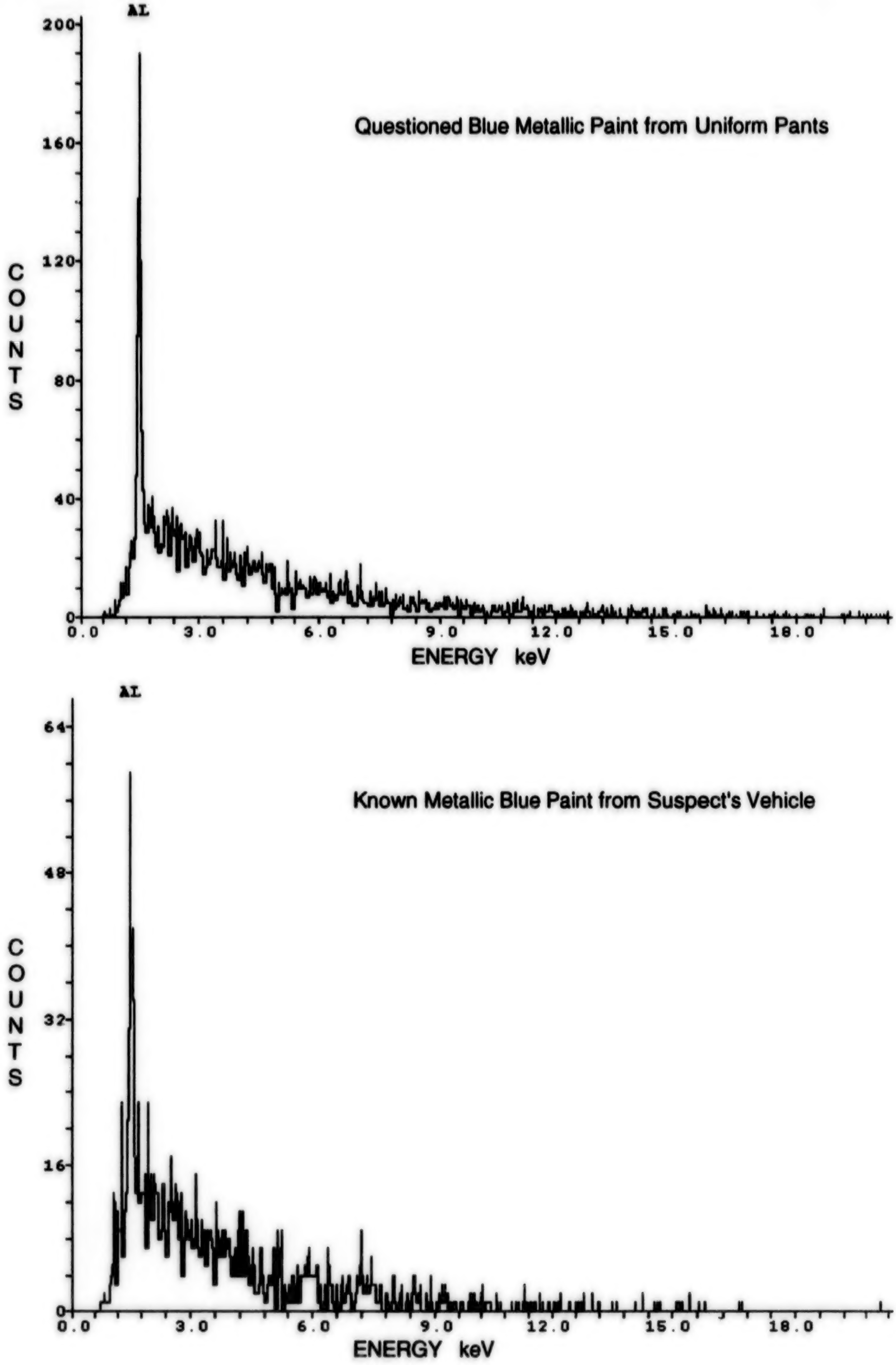


Figure 18. EDX spectra of the questioned blue metallic paint from the trooper pants and the known paint sample from the suspect's vehicle.

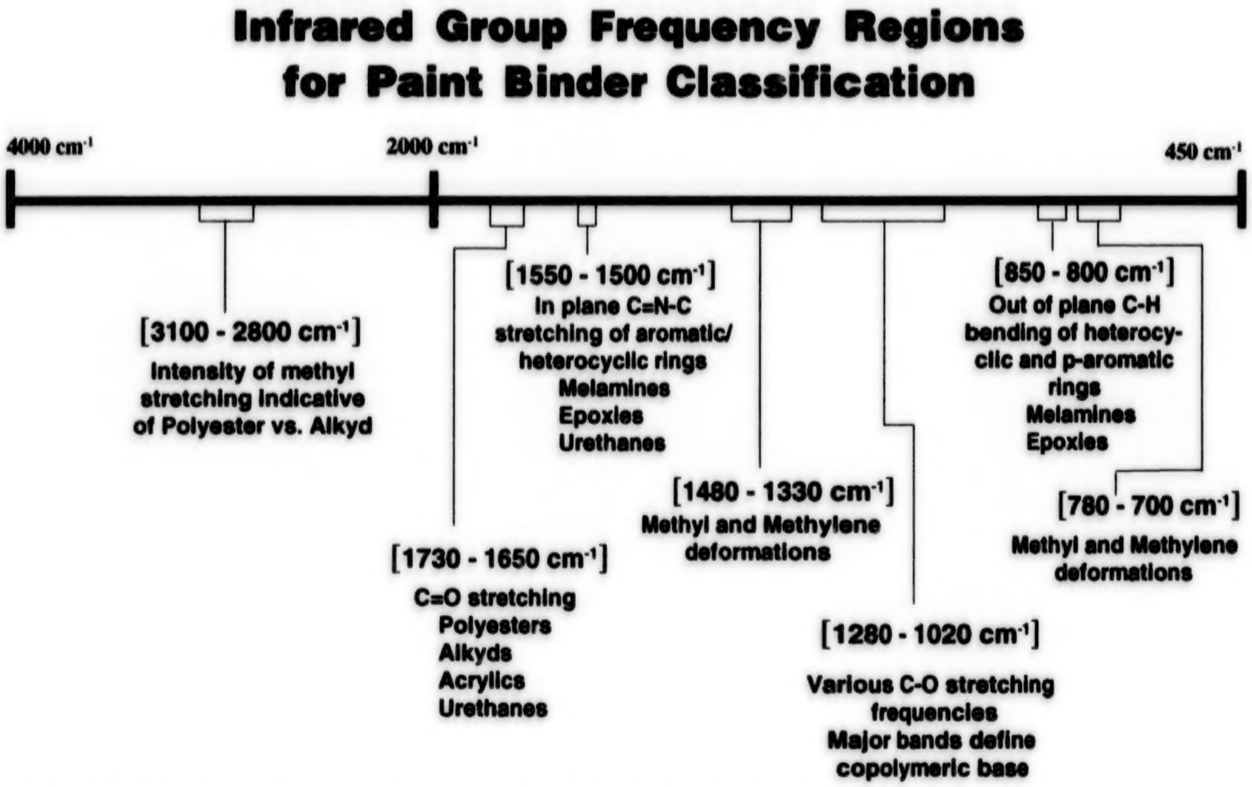

Infrared Group Frequency Regions for Paint Binder Classification
4000 cm⁻¹
2000 cm⁻¹
450 cm⁻¹
[3100 - 2800 cm⁻¹]
Intensity of methyl stretching indicative of Polyester vs. Alkyd
[1550 - 1500 cm⁻¹]
In plane C=N-C stretching of aromatic/ heterocyclic rings
Melamines
Epoxies
Urethanes
[850 - 800 cm⁻¹]
Out of plane C-H bending of heterocyclic and p-aromatic rings
Melamines
Epoxies
[1480 - 1330 cm⁻¹]
Methyl and Methylene deformations
[780 - 700 cm⁻¹]
Methyl and Methylene deformations
[1730 - 1650 cm⁻¹]
C=O stretching
Polyesters
Alkyds
Acrylics
Urethanes
[1280 - 1020 cm⁻¹]
Various C-O stretching frequencies
Major bands define copolymeric base

Figure 19. Major infrared group frequency regions used in spectral identification of automotive paint polymers.

bers from the CTS file name (Table 6) are used to retrieve their respective color panels for visual color comparison. Figure 23 shows a visual color comparison of color panel 1199 (second hit in search results) against the questioned blue metallic paint removed from the trooper's pants. As can be seen, and as is corroborated by the results of microspectrophotometric examinations (Figure 24), there are no color differences between the known color panel and the questioned sample. Next, in the CTS Reference document locate the color number 1199 and a list of vehicle models and years in which this color was used (Table 5). Table 5 shows that one of the vehicle models painted with color 1199 was a 1986 Oldsmobile Firenza, the year and model of the suspected hit and run vehicle submitted to the laboratory for examination (Figure 25).

Table 4. TEST SAMPLES AND SEARCH RESULTS

SEARCH HIT SELECTION NUMBERS	1	2 - 4	5 - 8
CTS PAINT COLLECTION (New Samplings)	9	1	0
SALVAGE YARD SPECIMENS	3	4	3
CASE SAMPLES	1	2	0
TOTALS	**13**	**7**	**3**
TOTAL TESTS + 23	57%	30%	13%

SUMMARY

In summary, some of the problems the forensic paint analyst faces and some techniques and methods to aid in their solution have been presented. From even thin smears of abraded paint, proper analytical procedures can determine the chemical binder and often the pigment type. Combining this information with microscopic observations and solubility results, the analyst can determine whether the paint is domestic, foreign, refinish or OEM. In cases of domestic OEM paint, further evaluation using the automotive paint data base and the CTS Automotive Paint Color Collection, can provide years, makes and models on which the paint has been used.

Paint evidence most often provides the judicial system with circumstantial evidence. A thorough multi-systems characterization, coupled with sound interpretations of data however, can provide the legal community with both valuable investigative information and significant judicial evidence.

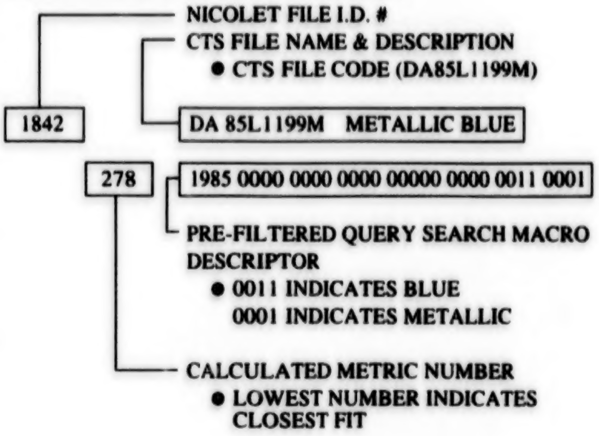
Table 5. SEARCH RESULTS OF CASE EXAMPLE AND EXPLANATION

Search Results

GBI PAINT CHIP LIBRARY - 3/88
POSSIBLE HITS

1850		PB85L1205M METALLIC BLUE
	273	1985 0000 0000 0000 00000 0000 0011 0001
1842		DA85L1199M METALLIC BLUE
	278	1985 0000 0000 0000 00000 0000 0011 0001
601		DB79L0345M METALLIC BLUE
	279	1979 0000 0000 0000 00000 0000 0011 0001
1849		NB85L1205M METALLIC BLUE
	279	1985 0000 0000 0000 00000 0000 0011 0001
560		DB77L0336M METALLIC BLUE
	280	1985 0000 0000 0000 00000 0000 0011 0001

EXPLANATION OF SEARCH RESULTS


NICOLET FILE I.D. #
CTS FILE NAME & DESCRIPTION
● CTS FILE CODE (DA85L1199M)
1842
DA 85L1199M METALLIC BLUE
278
1985 0000 0000 0000 00000 0000 0011 0001
PRE-FILTERED QUERY SEARCH MACRO DESCRIPTOR
● 0011 INDICATES BLUE
0001 INDICATES METALLIC
CALCULATED METRIC NUMBER
● LOWEST NUMBER INDICATES CLOSEST FIT

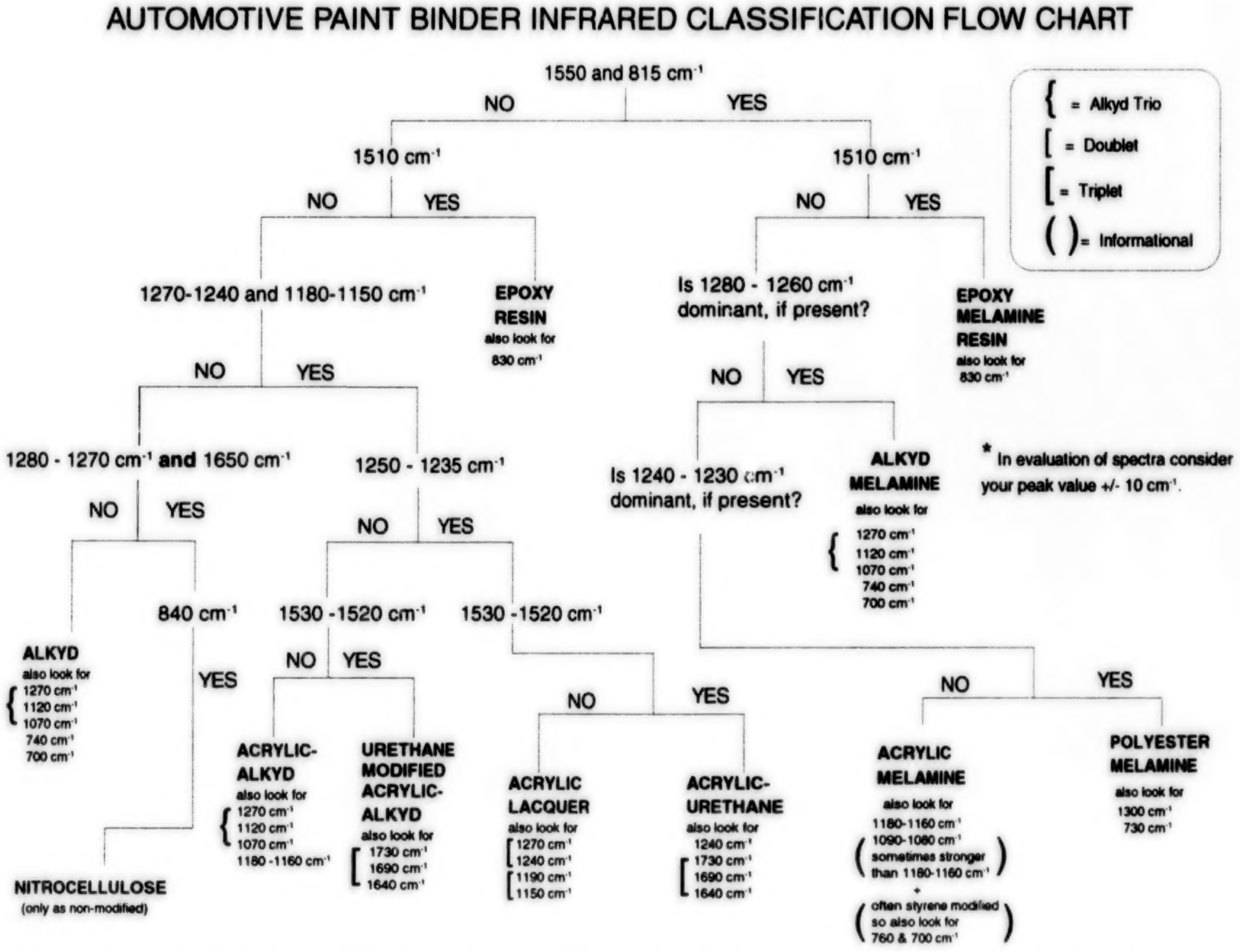


Figure 20. Flow chart used for infrared spectral interpretation of automotive paint polymers to assist analyst in identifying 11 major binder types.

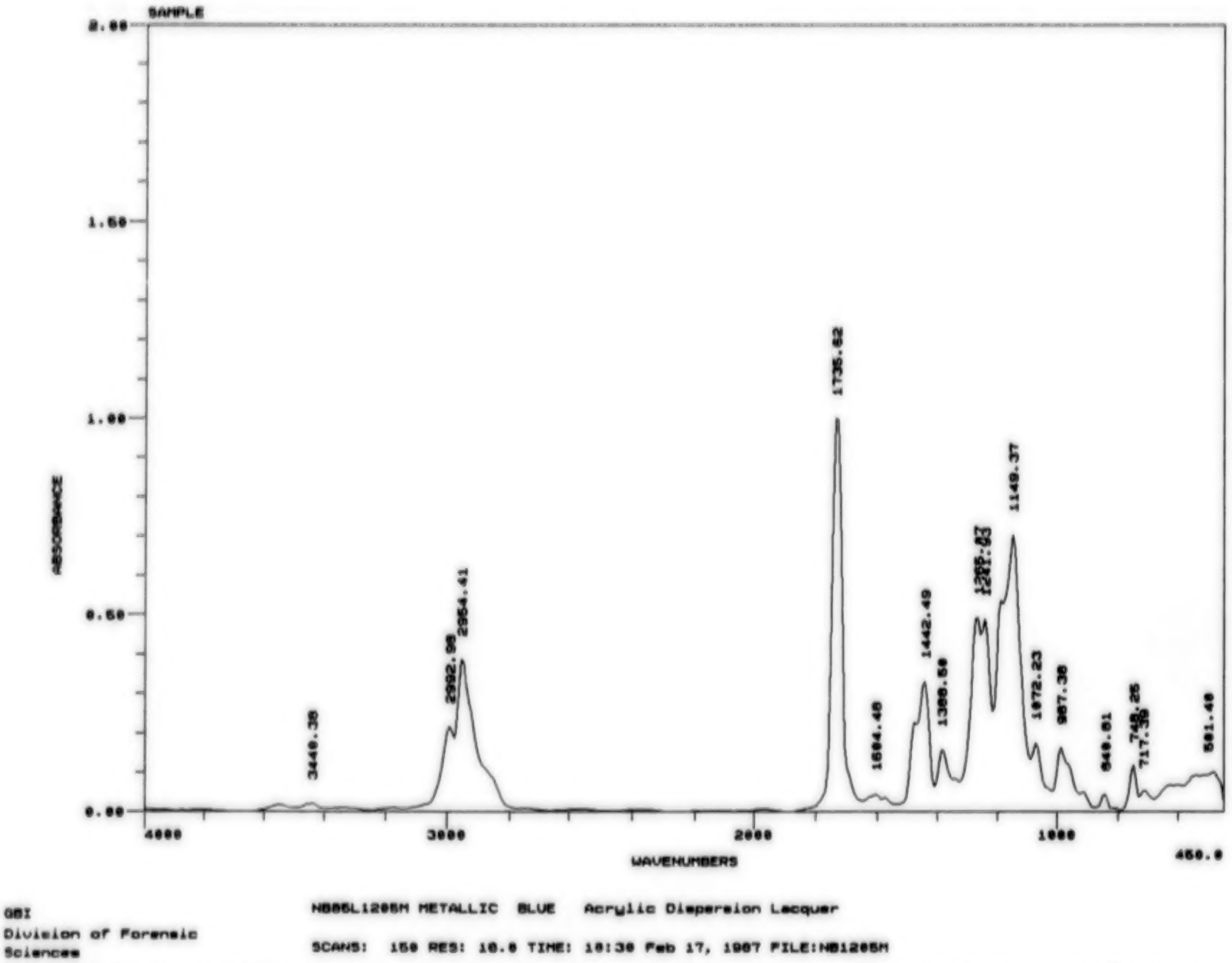


Figure 21. Infrared spectra of four typical automotive paint polymers (A) acrylic dispersion lacquer, (B) acrylic melamine enamel, (C) polyester melamine enamel, and (D) urethane modified acrylic-alkyd.

Table 6. CTS PAINT REFERENCE COLLECTION DOCUMENT USED TO LOOK UP COLOR NUMBER

**Color: 1199 Appear: METALLIC Mfg: GENERAL MOTAORS Mfg Ref Num: WA8574

This color used on	Paint (supplier-type-year-location)
87 BUIC-CENTURY, LE SABRE, REGAL	**DA85C, DB85B, PB85C**
87 CADI-CIMARRON	**DA85C, DB85B, PB85C**
87 CHEV-CAPRICE, CELEBRITY, CHEVETTE, IMPALLA, MALIBU, MONTE CARLO	**DA85C, DB85B, PB85C**
87 OLDS-CUTLASS SIERA, CUTLASS SUPREME, DELTA 88	**DA85C, DB85B, PB85C**
87 PONT-6000, GRAND PRIX, SAFARI WAGON, T1000	**DA85C, DB85B, PB85C**
86 BUIC-CENTURY CUSTOM, ESTATE WAGON, REGAL, SKYHAWK, SKYLARK	**DB85C, DB86B, PB85C**
86 CADI-CIMARRON, FLEETWOOD	**DB85B, NB86C, PB85C**
86 CHEV-CALALIER, CAPRICE, CELEBRITY, CHEVETTE, CITATION, IMPALA, MALIBU, MONTE CARLO	**DB85B, NB86C, PB85C**
86 OLDS-CUTLASS SIERA, DELTA 88, FIRENZA	**DB85B, NB86C, PB85C**
86 PONT-6000, BONNEVILLE, GRAND PRIX, J200, PARISIENNE, T100	**DB85B, NB86C, PB85C**
85 BUIC-CENTURY, ESTATE WAGON, REGAL, RIVIERA, SKYHAWK, SKYLARK	**DA85C, DB85B, NB85C, NW85C, PB85C**
85 CADI-CIMARRON, EL DORADO, SEVILLE	**DA85C, DB85B, NB85C, NW85C, PB85C**
85 CHEV-CAVALIER, CAPRICE, CELEBRITY, CHEVETTE, CITATION, IMPALA, MALIBU, MONTE CARLO	**DA85C, DB85B, NB85C, NW85C, PB85C**
85 OLDS-CUTLASS SIERA, CUTLASS SUPREME, DELTA 88, FIRENZA, TORONADO	**DA85C, DB85B, NB85C, NW85C, PB85C**
85 PONT-6000, BONNEVILLE, GRAND PRIX, J2000, PARISIENNE, T1000	**DA85C, DB85B, NB85C, NW85C, PB85C**

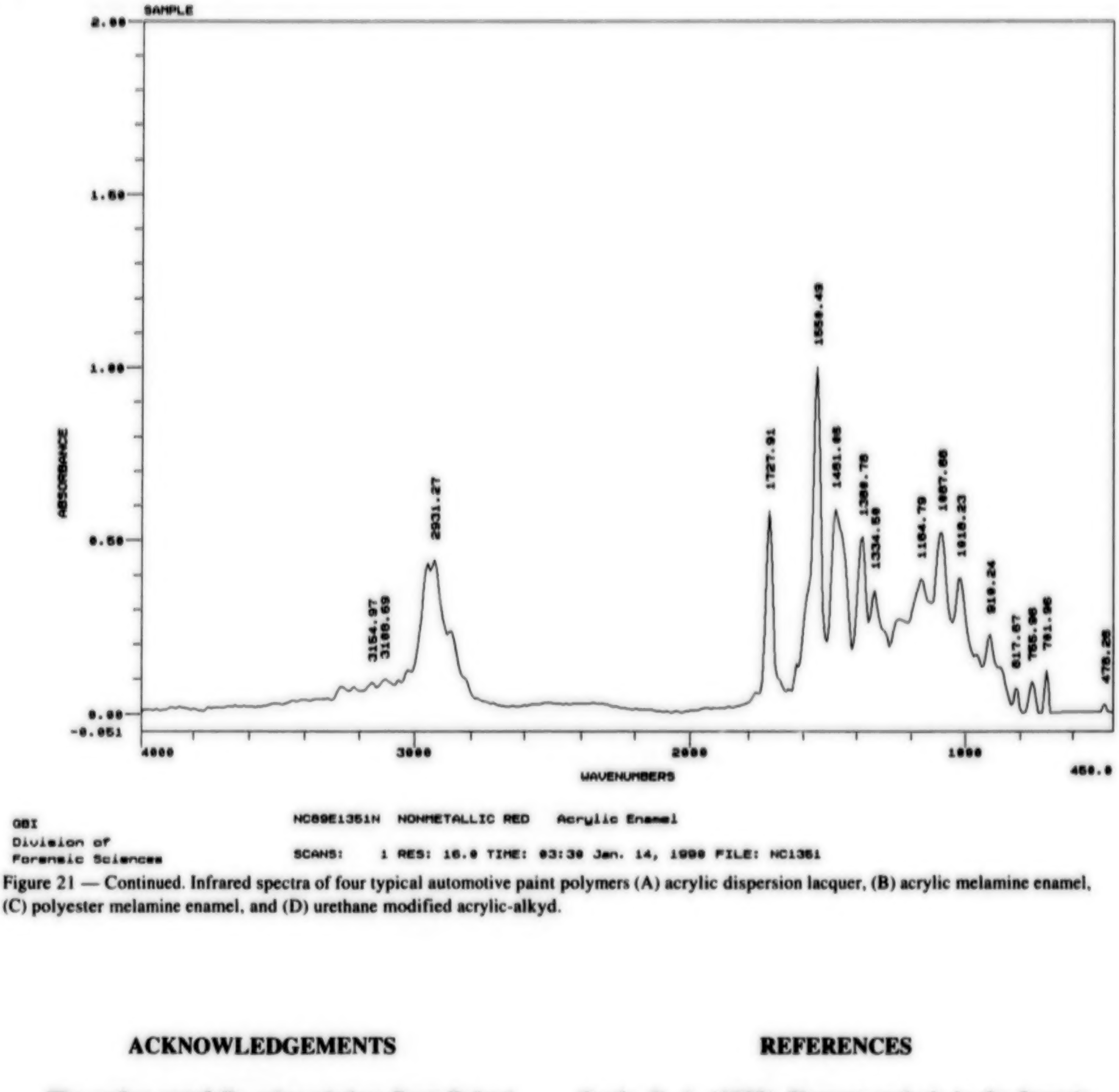


Figure 21 — Continued. Infrared spectra of four typical automotive paint polymers (A) acrylic dispersion lacquer, (B) acrylic melamine enamel, (C) polyester melamine enamel, and (D) urethane modified acrylic-alkyd.

ACKNOWLEDGEMENTS

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REFERENCES

Castle, D. A. (1982). Pigment analysis in the forensic examination of paints. II. Analysis of motor vehicle paint pigments by chemical tests, J. Foren. Sci. Soc. 22:179-186.

Cousins, D. R., Platoni, C. R. and Russell, L. W. (1984a). The use of microspectrophotometry for the identification of pigments in small paint samples, Foren. Sci. Int. 24:183-196.

Cousins, D. R., Platoni, C. R. and Russell, L. W. (1984b). The variation in the colour of paint on individual vehicles, Foren. Sci. Int. 24:197-208.

Crown, D. A. (1968). The Forensic Examination of Paints and Pigments, Charles C. Thomas Publ., Springfield, IL, pp. 24-54.

Laing, D. K., Dudley, R. J. and Isaacs, M. D. J. (1980). Colorometric measurements on small paint frag-

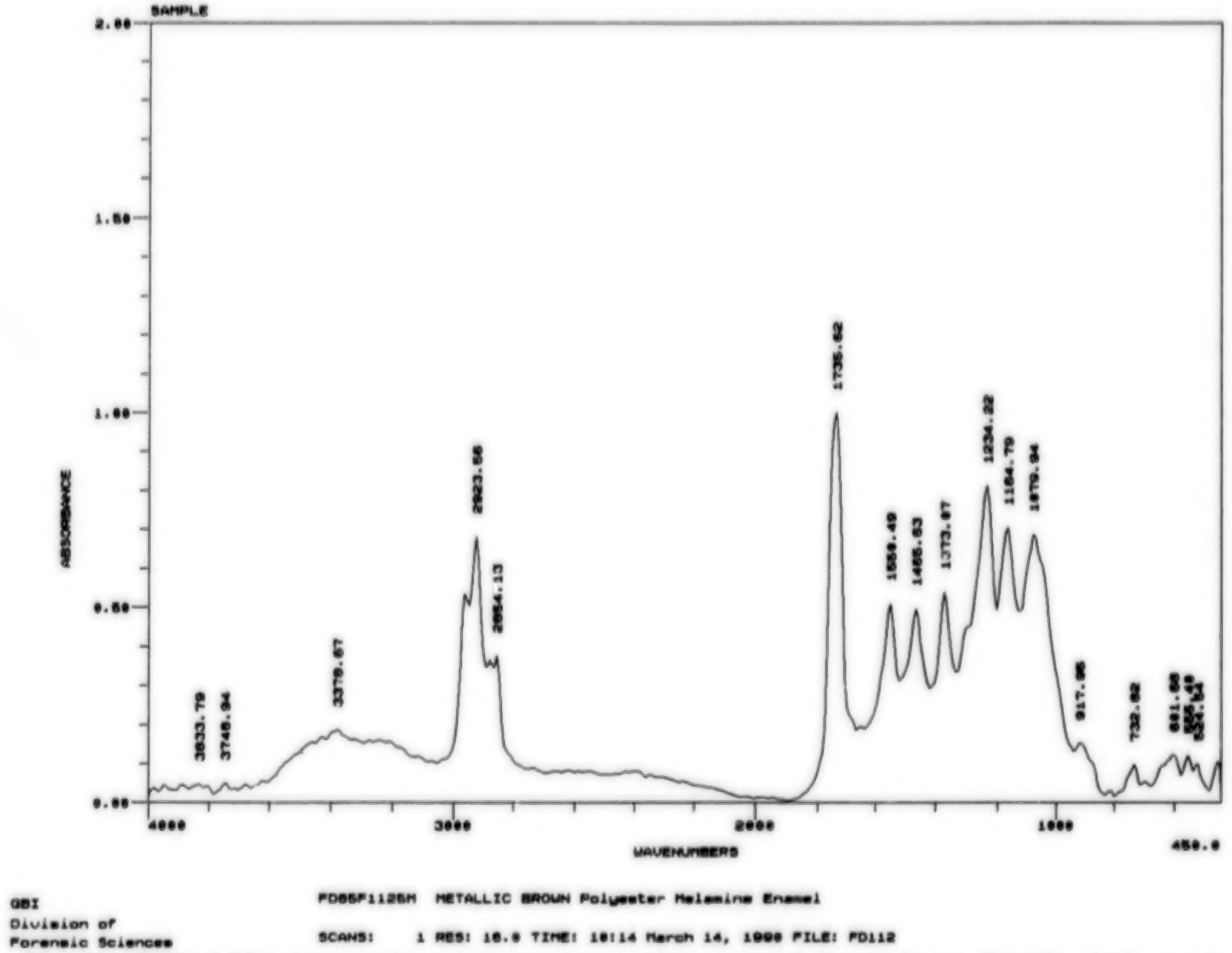
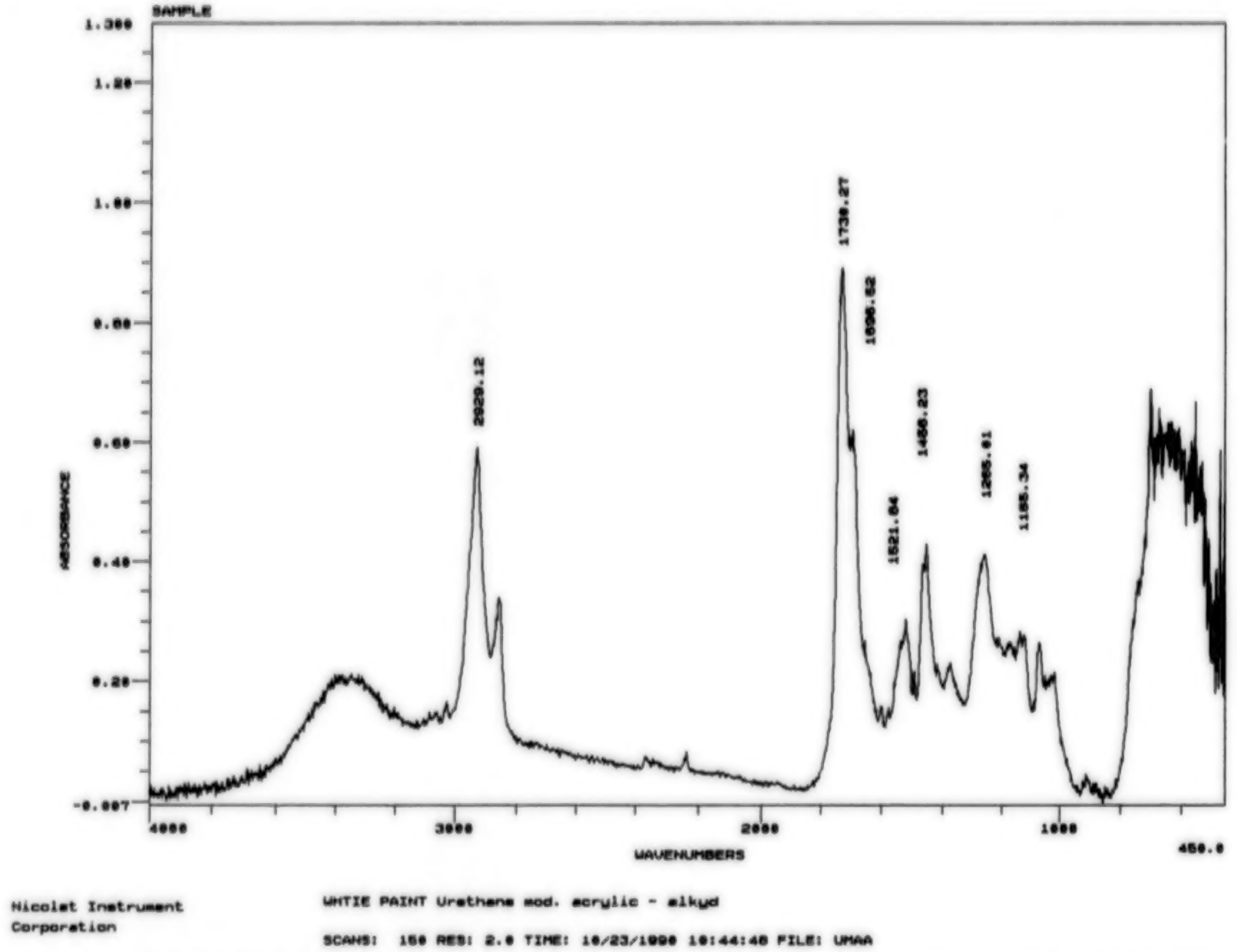


Figure 21 — Continued. Infrared spectra of four typical automotive paint polymers (A) acrylic dispersion lacquer, (B) acrylic melamine enamel, (C) polyester melamine enamel, and (D) urethane modified acrylic-alkyd.



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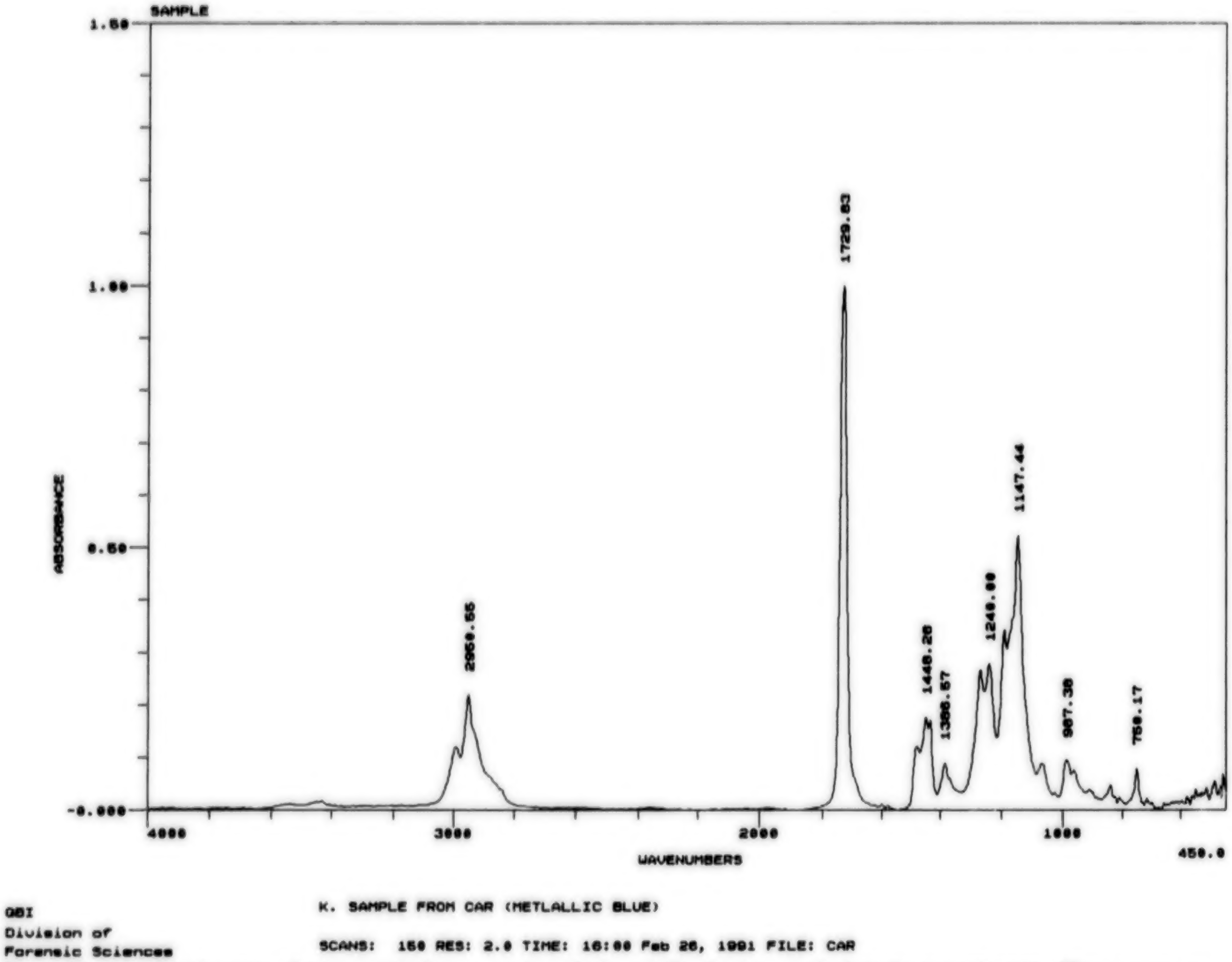

Figure 22. (A) Infrared spectra of paint sample from suspect's vehicle and (B) of paint sample from the trooper's pants. These spectra are interpreted as acrylic lacquers.

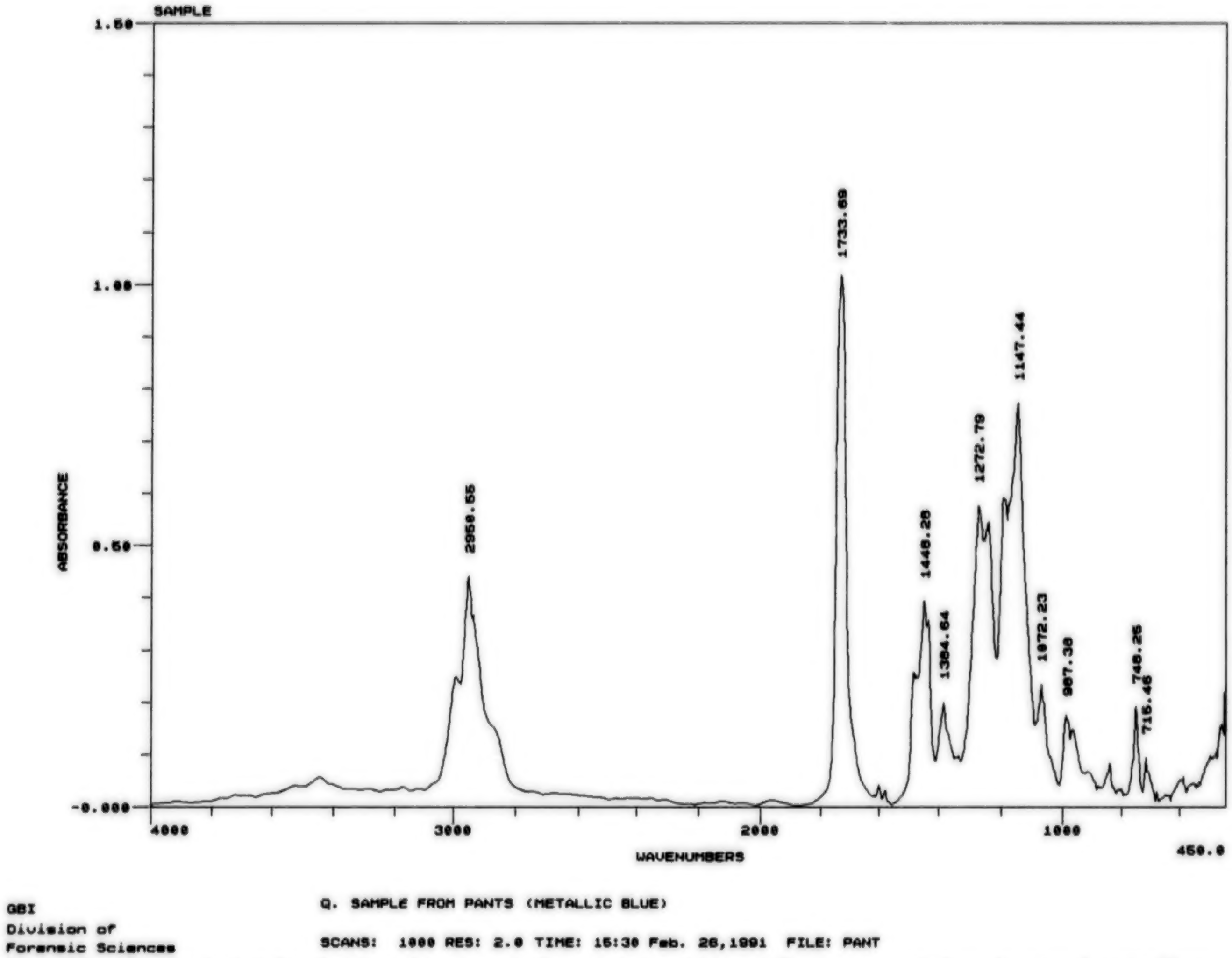

Figure 22 — Continued. (A) Infrared spectra of paint sample from suspect's vehicle and (B) of paint sample from the trooper's pants. These spectra are interpreted as acrylic lacquers.

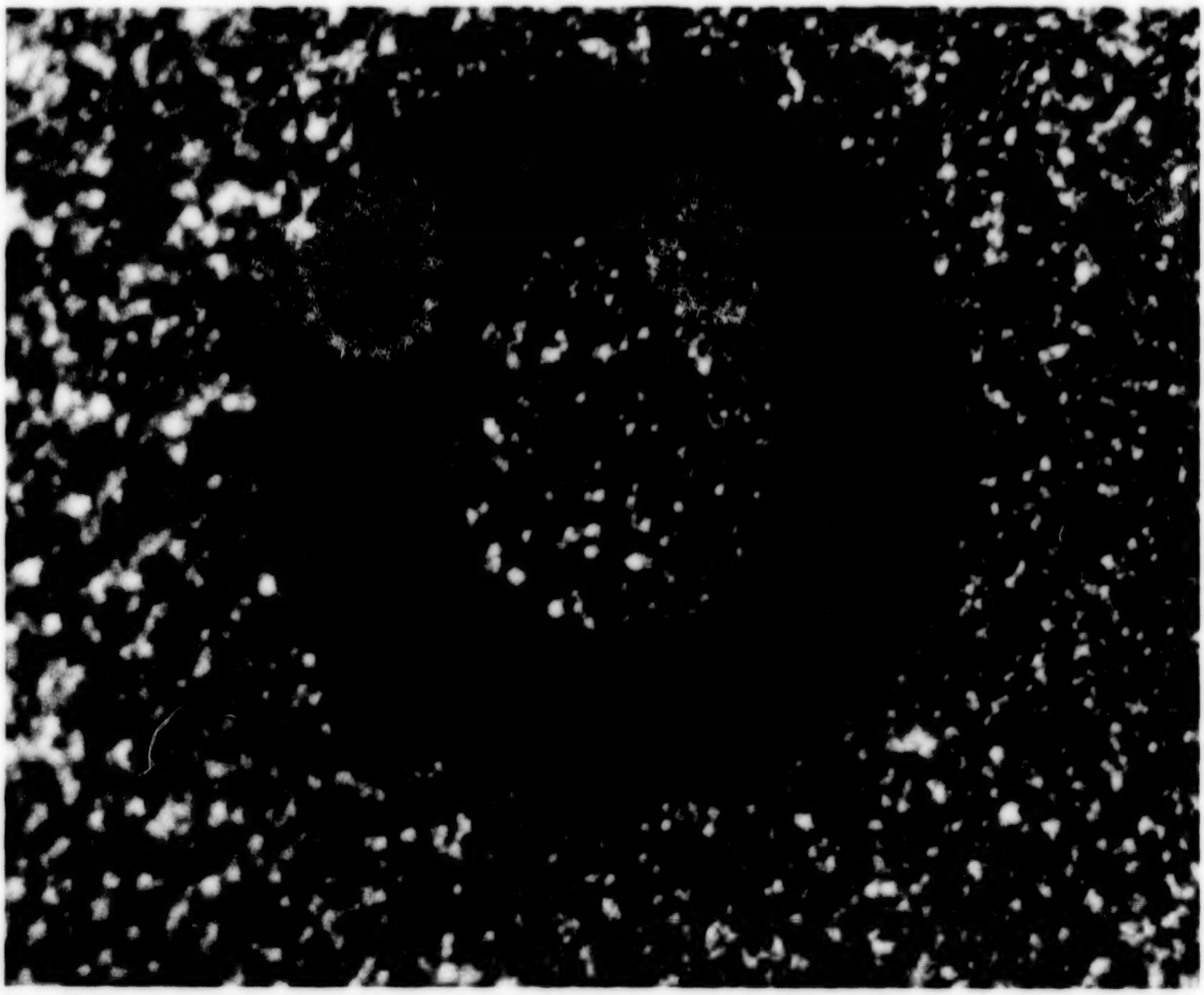

Figure 23. Photomicrograph showing a visual color comparison of a small sample of questioned blue metallic paint against color panel 1199 from the CTS Collection. The arrow points to the questioned sample (70X).

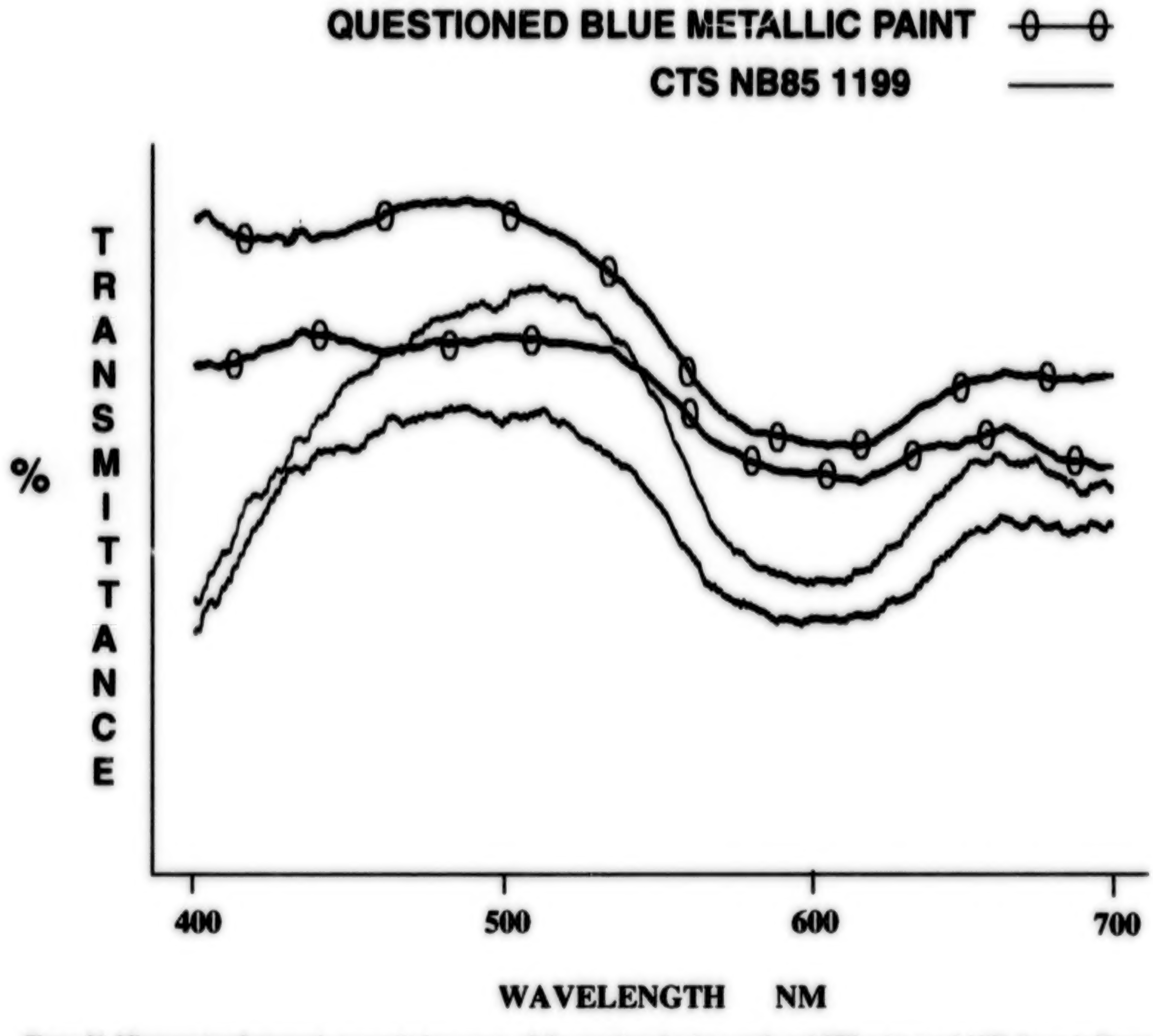

Figure 24. Microspectrophotometric transmission curves of the questioned paint sample and CTS paint panel 1199 shown in Figure 23.

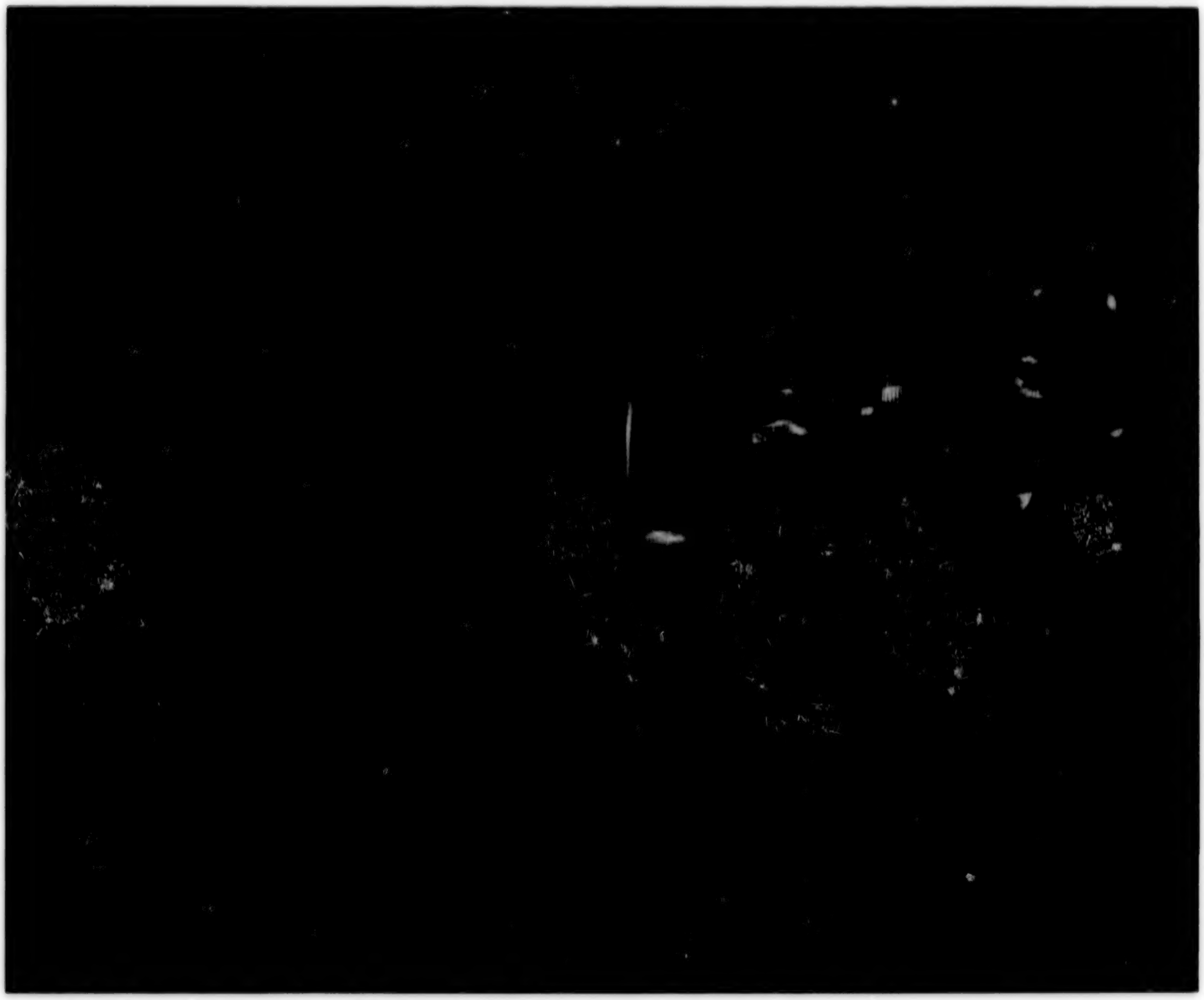

Figure 25. Photograph of the suspect's 1986 Oldsmobile Firenza.

ments using microspectrophotometry, Foren. Sci. Int. 16:159-171.

Laing, D. K., Dudley, R. J., Home, J. M. and Isaacs, D. J. (1982). The discrimination of small fragments of household gloss paint by microspectrophotometry, Foren. Sci. Int. 20:191-200.

Nowicki, J. and Patten, R. (1986). Examination of U.S. automobile paints: I. Make and model determination of hit-and-run vehicles by reflectance microspectrophotometry, J. Foren. Sci. 31:464-470.

Percy, R. F. E. and Audette, R. J. (1980). *Automotive repaints: just a new* look? J. Foren. Sci. 25:189-239.

Reeve, V., Mathiesen, J. and Fong, W. (1976). Elemental analysis by energy dispersive x-ray: a significant factor in forensic analysis of glass, J. Foren. Sci. 21:291-306.

Rogers, P. G., Cameron, R., Cartwright, N. S., Clark, W. H., Deak, J. S., and Norman, E. W. W. (1976a). The classification of automobile paint by diamond window infrared spectrophotometry part I: binders and pigments, J. Can. Soc. Foren. Sci. 9:1-14.

Rogers, P. G., Cameron, R., Cartwright, N. S., Clark, W. H., Deak, J. S., and Norman, E. W. W. (1976b). The classification of automobile paint by diamond window infrared spectrophotometry part II: automotive topcoats and undercoats, J. Can. Soc. Foren. Sci. 9:49-68.

Ryland, S. G., Kopec, R. J. and Somerville, P. N. (1981). The evidential value of automobile paint. Part II: Frequency of occurrence of topcoat colors, J. Foren. Sci. 26:64-74.

Thornton, J. I. (1981). Forensic paint examination. In: Forensic Science Handbook, (Saferstein, R., ed.). Prentice-Hall, NJ, pp. 529-571.

Thornton, J. I., Kraus, S., Lerner, B. and Kahane, D. (1983). Solubility characterization of automotive paints, J. Foren. Sci. 28:1004-1007.

Tillman, W. L. and Bartick, E. G. (1990). The evaluation of an infrared spectroscopic automobile paint data base, 12th Intl. Meeting Foren. Sci., Adelaide, Australia, Oct. 24-30.21.

THE APPLICATIONS OF MULTIELEMENTAL ANALYSIS IN TRACE EVIDENCE EXAMINATIONS

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The varied nature of crime leads to the possibility of almost any type of material being submitted to a forensic science laboratory for examination and analysis, with the aim of revealing whether a crime has in fact been committed, in what manner, and possibly at what time. Although scientific evidence will rarely by itself be sufficient to convict a suspected person, it is often of value in establishing a link between the suspect and an object or place. Contact traces, either of material left at the scene of the crime by the suspect, or some evidence associated with the crime scene that has been transferred to the suspect or to his or her clothing, can provide this link.

For many years the examination of contact traces has been an important part of the work carried out in forensic science laboratories, and it is usually associated with offenses against the person, thefts, breaking offenses, or with the hit and run type of road traffic accident. In addition to physical evidence such as blood, fibers, wood, vegetation, soil, metal, glass and paint, contact traces may be present in the form of marks, for example, fingerprints, shoeprints and tiremarks, or indented impressions such as toolmarks and bitemarks.

From the perspective of a forensic scientist working a quarter century ago Walls (1968) stated that glass, paint and soil were the most commonly encountered forensic trace evidential materials, and he advocated their chemical analysis. The emphasis of forensic examinations has changed considerably since 1968, and chemical analysis of contact traces has fallen somewhat from vogue in recent years, perhaps due to the inability of such analyses to provide evidence that is as positive as, for example, the finding of a matching fingerprint, shoeprint or toolmark. Scene examiners will often look for shoeprints or toolmarks, after an initial examination for fingerprints has been made, in preference to collecting paint or glass samples. Nevertheless, chemical analysis of contact traces can, and often does, provide important supporting evidence.

In the space available to this paper it is not possible to provide a complete review of how the various techniques of multielemental analysis are applied to analyzing the complete range of trace evidential material (Table 1). Therefore, one specific type of material, glass, is selected as an example. Whilst the principal analytical techniques are covered in respect of their use for the analysis of glass, the fullest descriptions are reserved for the various techniques based on atomic spectroscopy.

GLASS AS TRACE EVIDENCE

Glass is an important contact trace material (Maehly and Stromberg 1981), and is commonly encountered as evidence in burglaries. Burglaries and robberies, although missing the media attention of major crime such as murder and rape, are in fact the offenses which are of most concern to the general public in the United Kingdom, and as such must be investigated thoroughly. During 1990 there were 173,200 instances of burglary in the Metropolitan Police District. Although 28% of these were walk in burglaries where the perpetrators did not need to make a forcible entry, there was still a very considerable number of forcible entries to houses, apartments and non-residential buildings. Many of these burglaries would have involved the breaking of glass.

Glass can of course appear as evidence in cases other than burglaries, for example, in incidents involving automobiles, or from assaults with a broken bottle. In recent years there has been a number of product tampering cases where the recovery and examination of glass fragments has been an important part of the overall investigation. Extracting the maximum possible evidential information from glass should therefore be considered a crucial and worthwhile aim for forensic science.

At speeds of 500 frames per second, films of people breaking glass show particles of glass flying backwards

Table 1. TRACE EVIDENTIAL MATERIAL IN FORENSIC SCIENCE

Pure metals	Blood	Mineral acids
Alloys	Urine	Organic solvents
	Tissue	
	Hair	
Foodstuffs		Water
Beverages		Gunshot residues
	Glass	
	Paint	
Soils		
Rocks		

from all parts of the window where cracks appear - not just from where the first puncture was made. This backward fragmentation (Zoro 1983) results in the breaker of a window being subjected to a shower of minute glass particles from the surface nearer to him. Whilst larger fragments will fall or be shaken from clothing within minutes, the smaller fragments may remain on the breaker's clothing for periods up to several hours.

Good forensic evidence can result if glass found on a suspect proves to be indistinguishable from the broken window at the scene of crime, and the items submitted to a forensic science laboratory in a typical case of burglary will be a control sample from a broken window and articles of clothing (and possibly combings of hair) from the suspect. Examination of the suspect's samples (Pounds and Smalldon 1978; Harrison *et al.* 1985) may lead to the recovery of glass fragments. The number and distribution of these are most important: the evidential value of a piece of glass embedded in the sole of a shoe should be assessed carefully (Walsh and Buckleton 1986), whereas the presence of many small fragments of glass on a shirt or sweater can be highly significant.

The following questions will need to be answered in cases involving glass as evidence:

> Firstly, is the sample glass? If so, what type of glass is it? - this is the problem of classification. If both control and suspect samples are submitted, then the further question of discrimination will arise. Although the forensic scientist should be capable of identifying all types of glass, the type of glass which is encountered most often in forensic casework is flat glass. It is not sufficient, however, to have data collections comprising solely flat glass, since it is sometimes necessary to identify total unknowns, for example, in product tampering cases. Additionally, it may be necessary to rebut a defence claim that, for example, the glass on the suspect's clothing came from a broken beer mug and not from a broken window.

The Composition of Glass

Glass is one of the oldest of all manufactured materials: a simple fusion of sand, soda and lime - all opaque substances - produces, when cooled, a transparent solid. This super-cooled liquid is rigid and fundamentally fragile, although by varying its composition it can be made relatively strong.

The majority of glasses have silicon, boron or phosphorus as the glass-forming element, with silicon glasses being the most common. Stabilizers such as CaO, MgO, BaO and especially Al_2O_3 are added to silica-based glasses to provide chemical resistance, whilst fluxes, generally oxides of the alkali metals, improve the melting properties of the glass but have low chemical resistance.

Chemical decolorization may be necessary if iron, present as an impurity in the raw materials, has imparted an unwanted color to the glass. Oxidants such as nitrates, sulphates, chlorates, arsenic, manganese or fluoride are added to convert any iron present to the Fe^{3+} state since the blue color of Fe^{2+} is much more intense than the yellow of Fe^{3+}. Physical decolorization also involves the addition of chemicals (such as Ni, Se, Co, Mn or Nd) but here they act by imparting to the glass a color which cancels out the iron coloration.

Glasses having widely different properties can be produced by varying the proportions of the stabilizers, fluxes and other additives, and there are currently over 700 glass compositions in commercial use.

Types of Glass in Everyday Use

A convenient division of glasses is according to usage: window, container, tableware, headlamp, etc. Flat glass is the generic term for the glass used in windows and doors although it is often referred to as sheet glass. Until the late 1950s flat glass was produced entirely by the Sheet and Plate processes. In 1959 the U. K. company Pilkington Brothers introduced the Float process in which molten glass is floated over a bath of molten tin to produce a distortion-free sheet. The production of float glass has since been licensed to 31 manufacturers in 21 countries and the manufacture of glass by the Sheet process has been virtually eliminated in the developed world.

PHYSICAL METHODS FOR THE FORENSIC EXAMINATION OF GLASS

Refractive index (RI) and density measurements have been used routinely in forensic science laboratories for many years and are still used extensively. Since RI and density are highly correlated with each other, it has been found sufficient to measure only one of these parameters on a routine basis. Modern instrumentation provides extremely sensitive methods for determining RI, and most forensic science laboratories prefer to measure this parameter. The discrimination afforded by RI measurement is impressive, but the technique is of limited use for classifying glasses due to the overlap of the RI distributions for the various types of glass, for example, flat glass and container glass (Figure 1).

Advances in microscopic techniques have enabled forensic scientists to establish whether minute glass fragments carry a portion of the original surface of the parent

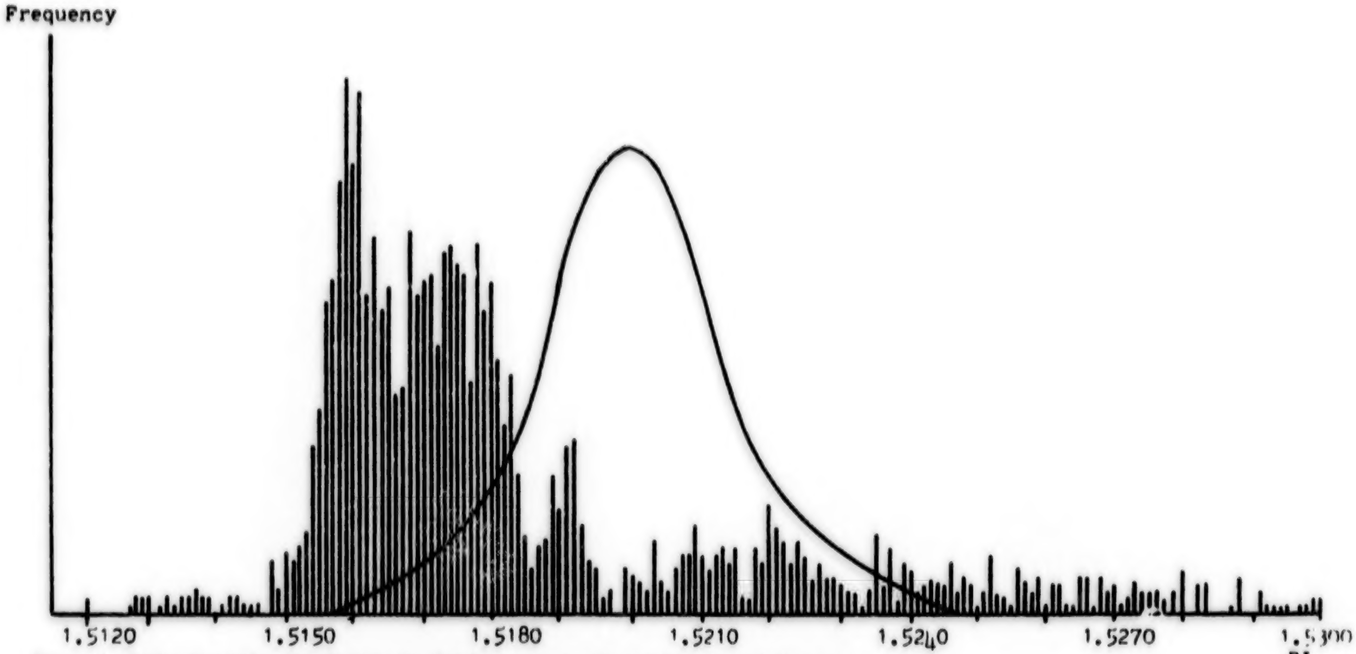


Figure 1. Refractive index distributions for flat (histogram) and container (curve) glasses.

object, and this can indicate the type of glass, for example, flat, or curved or mould blown (Goodwin *et al.* 1985). Welch *et al.* (1989) found that the presence of light and dark bands in microscopic glass fragments appeared to be related to the manufacturing process.

Marcouiller (1990) was able to separate tempered glass from other common glass types by an annealing method.

Many glasses, when excited by ultra-violet radiation, exhibit fluorescence in the visible region, and such spectra can be used to differentiate between float and non-float glasses.

CHEMICAL METHODS FOR THE FORENSIC EXAMINATION OF GLASS

Information available from chemical analysis can provide very useful data. In particular, the concentrations of most trace elements in glass are not correlated with RI or density and therefore, in terms of discrimination, elemental analysis has the potential to increase the evidential value of glass. Determining various elements in glass can also provide the basis of successful procedures for classifying glasses.

With the dual aims of classifying and discriminating glass samples, it is likely that several elements should be determined.

An ideal classifying element will be one having a distinct concentration range for each class of glass, and useful elements should be those that are varied intentionally by the glass manufacturer, that is, the major and minor components. For example, Pilkington has, since 1930, closely monitored the level of Mg added to flat glass to control the properties of the molten glass. The Mg content of flat glass will be higher than either container or tableware glass. In contrast, container glasses may have higher concentrations of As than other types of glass since this element is sometimes utilized as a batch refining agent for container glass.

Good discriminating elements for any particular class of glass will be those having wide concentration ranges when compared to the analytical sensitivities (defined as the ability to determine, with confidence, differences in concentration). It is possible that such elements will be trace impurities that enter the glass from the raw materials, since the concentrations of many of these impurities are unlikely to be controlled by the glass manufacturer. The use of locally-available raw materials will produce some variation in the levels of the trace constituents: German and Scaplehorn (1972) have reported that two Pilkington plants in the U. K. were characterized by the levels of Sr and Rb in their products. If sufficient information and analytical data were ever to become available for the many types of glass in commercial production, then the possibility arises that elemental analysis could be used to identify a specific manufacturer.

Although elements identified as good for classifying glass samples might also be useful for discrimination purposes, a separate selection of elements will probably be required to achieve both good classification and good discrimination. In general terms, greater confidence in assessing discrimination will be provided by measuring as many variables as possible. For classification many variables should also give the best results, although it may be possible to achieve effective classification with a small number of variables, the addition of other variables contributing little extra information.

Sample Cleaning Prior to Chemical Analysis

Fragments of glass recovered in casework will usually have to be cleaned prior to analysis, and in this respect it is fortunate that glass is fairly resistant chemically, enabling a thorough washing procedure to be carried out. At the Metropolitan Police Forensic Science Laboratory we have used a standard washing procedure for a number of years: glass fragments are soaked in concentrated HNO_3 for a minimum of 30 min, rinsed three times with distilled water, followed by an ethanol rinse, and finally dried in an oven at 50-60ºC.

Methods of Elemental Analysis of Glass

A variety of chemical analysis techniques are of potential use for the analysis of glass. To be suitable for forensic purposes, however, a technique must be capable of rapidly determining several elements, some of which may be present in the glass at low concentrations (ppm level). The main limitation will be the requirement to analyze the size of glass fragments (tens of μg up to a few mg) that might be recovered from clothing (Pearson *et al.* 1971).

Analytical methods which provide quantitative data are preferred since these will allow comparisons to be made, not only between suspect and control samples, but also between these analyses and previously analyzed samples, or indeed to other workers' data, perhaps produced by a completely different analytical technique. If they are accurate, quantitative data will be time-independent and can be easily stored as computer files, accessible for various statistical procedures.

A brief review, with some key references, is given of the principal techniques employed to analyze glass. For atomic spectroscopy, the main examples are provided by the work carried out on glass analysis during the last 20 years at the Metropolitan Police Forensic Science Laboratory. Updating our analytical methodology has allowed the range of elements determined in glass to be improved, and the sample size for analysis has been reduced. In parallel to these developments in atomic spectroscopic techniques, scanning electron microscopy has been used to analyze glass, specifically for samples smaller than 100 μg, and for elements other than those determined by ICP-AES (Keeley and Christofides 1979).

Spark Source Mass Spectrometry

During the 1970's spark source mass spectrometry (SSMS) was investigated as an analytical technique at the Home Office Central Research Establishment at Aldermaston. German and Scaplehorn (1972) reported the relative levels of up to fifteen elements in eight samples of window glass, and Dabbs *et al.* (1973) analyzed twenty window glasses of RI 1.5157 - 1.5159 for twelve elements. Magnesium was not determined. In a survey of headlamp glasses (Butterworth *et al.* 1974), the elemental concentrations of fifteen elements were tabulated for a total of 29 lamps, the product of at least fourteen different British, Continental, American and Canadian manufacturers. A later paper (German *et al.* 1978) reported the results of a survey of British container glass and listed thirteen elemental concentrations for seventeen colorless containers from two major manufacturers, nine colorless containers from seven smaller firms, and twenty colored containers from a number of manufacturers. Several years work was summarized by Locke *et al.* (1978), but despite the multi-element approach of SSMS, it has not found any wide use in forensic science.

Isotope dilution SSMS has been applied to the determination of K, Rb, Sr, Zr and Ba in window glasses with relative standard deviations (RSDs) of approximately 6% (Haney 1977).

Neutron Activation Analysis

In the late 1960's neutron activation analysis enjoyed some popularity in forensic analysis, mainly due to the efforts of three or four groups of workers. In the United Kingdom Goode and Coleman at the Atomic Weapons Research Establishment at Aldermaston investigated neutron activation analysis for determining several elements in glass (Coleman and Wood 1968; Coleman and Goode 1973; Goode *et al.* 1969), and applied the technique to forensic casework (Coleman and Weston 1968). Ruch *et al.* (1964) at General Dynamics in San Diego, California, and Perkons and Jervis (1962) in Toronto, Canada, also made valuable contributions to this area of forensic analysis. Schmidt and Smith (1970) reported the use of neutron activation analysis for forensic glass analysis.

Electron Microprobe, Scanning Electron Microscopy, X-Ray Fluorescence

Whitney and MacDonell (1964) and Smale (1973) have reported the use of the electron microprobe for forensic purposes. Sample examination and analysis with the scanning electron microscope is now recognized as a valuable technique in forensic science, and its use is relatively widespread (Bradford and Devaney 1970; Keeley and Christofides 1979).

X-ray fluorescence provides a fast, non-destructive method of elemental analysis, and the simultaneous analysis of elements commonly present in glass (except B and O) can be readily achieved. The method is suitable for determining the major elements in small glass samples, although it has poor relative sensitivity, with a detection limit of about 0.1% (1000 ppm).

Although Vasan *et al.* (1973) employed wavelength dispersive X-ray analysis using a scanning electron microscope, energy dispersive X-ray analysis has proved a more popular technique: Korda *et al.* (1973), Reeve *et al.* (1976), Howden *et al.* (1978), and Keeley and Christofides (1979).

Atomic Spectroscopy

Atomic spectroscopy: classical emission spectrography: The first major item of analytical equipment to be acquired by the Metropolitan Police Forensic Science Laboratory, an Adam Hilger Ltd. medium quartz spectrograph, was purchased in 1946. For several years this instrument, with sample excitation in a direct current arc, was used to analyze virtually any material arising in casework. A previous Director of the Laboratory commented (Walls 1968): "the spectrograph has probably been on the whole the hardest worked analytical instrument in forensic science", but 25 years later the availability of a wide range of analytical instrumentation - infra-red and ultra-violet spectroscopy, gas and high-performance liquid chromatography, mass spectrometry, atomic spectrometry, X-ray fluorescence, X-ray diffraction, scanning electron microscopy - has radically improved the options available to forensic scientists.

Spectrography allowed, at any early stage in the development of instrumental techniques, the simultaneous multi-element analysis of a variety of substances, with the minimum of sample pretreatment, good detection limits and the production of a permanent record of the analysis. Although most often employed as a qualitative technique, it is possible to obtain fully quantitative results from emission spectrography if densitometry is carried out on selected elemental lines on the photographic plate, provided that suitable standards are analyzed alongside the casework sample(s).

As other instrumental techniques have been evaluated and brought into routine use, spectrography has been employed less frequently in forensic science. The Metropolitan Police Forensic Science Laboratory is no exception to this but, nevertheless, the original Hilger spectrograph is still in regular use.

The spectrographic procedure developed by Blacklock *et al.* (1976) was employed at the Metropolitan Police Forensic Science Laboratory from 1973 to 1976 for routine glass analysis. Six elements - Al, Ba, Ca, Fe, Mg and Mn - were quantitatively determined in glass samples weighing approximately 1 mg. Washed glass samples were added to 85 mg matrix mixture (200 mg CuO + 800 mg LiF + 5 g graphite) in an agate mortar. The mixture was ground until homogeneous, and was then transferred to a cup-type electrode and burnt to completion in a d.c. arc. A Hilger 3 m grating spectrograph was employed (although a Hilger medium quartz spectrograph was also used) and densitometry was carried out on the photographic plates using Cu as the internal standard (since this element only occurs in glass at very low levels). The procedure was very demanding on the operator and a trained analyst would take about four days to complete the analysis of six elements in twelve glass samples; the authors of the method pointed out that a direct reading spectrograph would allow more samples to be analyzed for more elements in a shorter time. The poor precision found for Fe was possibly due to random airborne contamination during the grinding step.

Early workers reported the application of emission spectrography to many sample types. For example Cerlon (1958) and Cregeen (1960) described its use in the examination of small samples for forensic purposes. Harvey (1968) reported a general method for the analysis of sub-mg samples for forensic purposes; some simple modifications to a standard d.c arc spectrograph enabled samples as small as 25-50 µg to be analyzed semi-quantitatively.

Butterworth (1974) has reported the use of the laser microspectral analyzer in emission spectroscopy.

Atomic spectroscopy: atomic absorption spectrometry: Atomic absorption spectrometry (AAS) will produce quantitative analyses, and generally it is the preferred technique when only a few elements are to be determined or when the concentration levels are too low for alternative analytical methods.

The two principal types of atom cell employed in AAS to provide thermal energy for sample vaporization and atomization are the premixed flame and the electrothermal atomizer.

In flame mode aqueous samples are usually nebulized directly using a pneumatic nebulizer/spray chamber combination, a method that generally requires a minimum sample volume of 3 ml. An alternative procedure, most commonly used for As and Se, is to generate hydrides with a reducing agent and to pass these into the flame. Higher sensitivity or selectivity can be achieved by pre-concentration (chelation/solvent extraction), and nebulizing the solvent directly into the flame. A techniques such as the one termed boat in flame, can be used for 10-100 µl samples. The discrete nebulization of µl volumes to give a peak absorbance reading with negligible loss in sensitivity can also be used.

Electrothermal atomization has the ability to handle small liquid samples (5-10 µl) with high sensitivity and ease of operation, but is somewhat slow. Matrix effects have been mitigated to some extent by the use of L'Vov platforms, pyrographite and chemical matrix modification.

The limitations of AAS in forensic glass analysis are that a number of dilutions of a dissolved glass sample may be necessary in order to determine several elements, and if electrothermal atomization is used the technique becomes increasingly time-consuming.

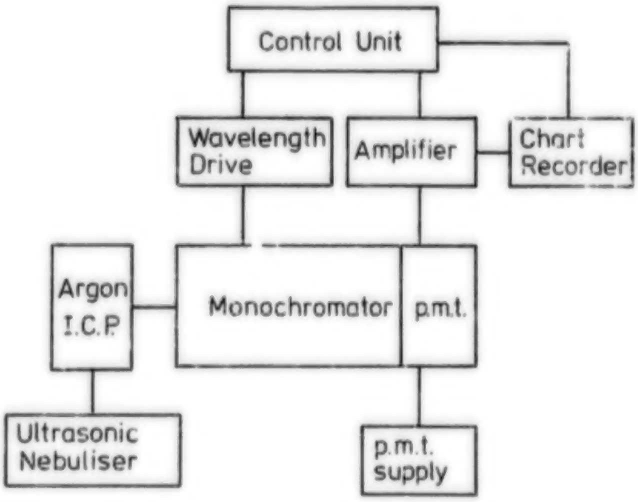
Atomic absorption spectrometric procedures for the analysis of glass were used routinely at the Metropolitan Police Forensic Science Laboratory from 1973 to 1979. In the method of Hughes *et al.* (1976) fragments of glass weighing 0.8 - 1.3 mg were digested in 1 ml (1HF + $1H_2O$) by agitating in an ultrasonic bath, resulting in a two-phase system containing a precipitate (which was predominantly CaF) and the supernatant solution. Manganese was determined at 279.5 nm by AAS with atomization in a graphite furnace, whilst atomization in an air - C_2H_2 flame was used for Mg (185.2 nm). Precisions were better than 10%, but even for just two elements the method was limited due to its slowness, since dilution of the sample solution and an electrothermal atomization procedure were involved.

Advances in digestion technique and instrumentation led to a rapid method for determining Mg, Fe and Mn in smaller fragments (200-500 µg) of glass (Catterick and Wall 1978). Washed glass samples were dissolved in 0.5 ml 1HF:2HCl acid mixture using agitation in an ultrasonic bath for 30 min, and the digest was diluted with 1.5 ml H_2O. Pulse nebulization of 200 µl aliquots (using a Teflon-lined nebulizer with a platinum-iridium capillary) allowed all three elements to be determined in this solution with relative standard deviations of 5-10%. The acid mixture used overcame the problem of low Mg (and Ca) levels which had been found when HF alone was used, either cold with ultrasonic agitation or at 110°C in a PTFE bomb, for digestion. The method was extended to the determination of Fe and Mg in samples as small as 100 µg.

A number of workers have, over the years, employed AAS for the analysis of glass samples, for example Jones (1965), Fuller and Whitehead (1974), Burdo and Wise (1975), and Wise and Solsky (1977). Howden *et al.* (1977) reported the satisfactory digestion of glass samples with HF alone in a PTFE bomb. The method allowed the analysis of a large number of samples on a routine basis and was claimed to be quicker and less arduous than previous electrothermal atomization - AAS procedures. Although often considered a single element technique, Kilroy and Moynihan (1978) utilized AAS in an analytical scheme for determining 16 elements in glass. A less conventional approach was employed by Headridge and Riddington (1984): solid sampling introduction into an induction furnace was used to determine Ag, Pb and Bi in glass samples by AAS.

Atomic spectroscopy: inductively coupled plasma - atomic emission spectrometry: The multi-element capability, good detection limits and large linear working ranges which are characteristic of plasma sources were considered extremely attractive for analyzing small fragments of glass. The difficulty of justifying expenditure without results led to our inductively coupled plasma - atomic emission spectrometric (ICP-AES) system being purchased and assembled in stages during a two-year period.

A schematic diagram of the original ICP-AES system is shown in Figure 2. It is based on a Radyne plasma source and torch and a sequential scanning system - since it was not known in advance which elements would be the most useful for forensic studies of glass, and the cost of a direct read spectrometer was considered pro-



Schematic diagram if ICP-AES system originally used at the Metropolitan Police Forensic Science Laboratory.

hibitive. A stepping motor, attached to the grating drive of a 1 m monochromator, is coupled to a unit, designed and built in-house, which controls the wavelength selection and the scanning interval and speed. The emission peaks are monitored using a small computer, the peak maxima are measured and stored, calibration graphs are constructed and the analysis results are calculated automatically, given the sample weights.

The ICP-AES method was developed from 1976, was published in 1979 (Catterick and Hickman 1979), and has been in routine use, with slight modifications, from 1979 to the present.

Glass samples are dissolved using a room-temperature digestion with the same acid mixture (1HF:2HCl) that was found effective for the AAS method (Catterick and Wall 1978). The desire to cope with these highly acidic solutions without further treatment (for example, with boric acid) and the necessity of a low uptake rate of sample solution into the plasma (to conserve sample solution, enabling small glass fragments to be analyzed) led to the selection of an ultrasonic nebulizer with an uptake rate of approximately 0.2 ml.min^{-1} (Table 2).

We have successfully employed the ultrasonic nebulizer design of Hoare *et al.* (1968) for a number of years (Figure 3). Ultrasonic energy from a Siemens Sonostat medical diathermy unit is transmitted to the sample solution in a polystyrene tube and the aerosol formed is swept by a stream of argon into the plasma. A PTFE tube placed inside the quartz sample tube of the plasma torch has been found effective in resisting HF attack on the quartz.

Table 2. OPERATING CHARACTERISTICS OF ULTRASONIC AND PNEUMATIC NEBULISERS

Type of nebuliser	Uptake rate ml.min.$^{-1}$	% of aerosol reaching plasma	Total % of sample made available for excitation
Pneumatic	~2 - 3 (natural ~0.4 - 1 (pumped)	10	10
Ultrasonic	~0.2	100	70

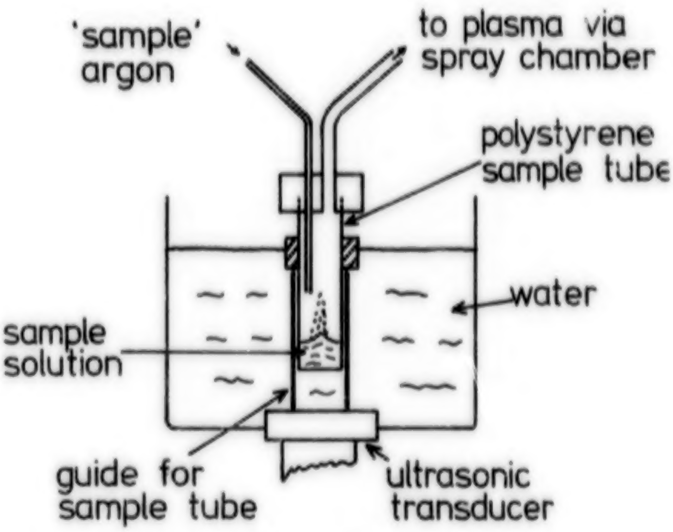


Figure 3. Ultrasonic nebuliser employed for ICP-AES.

The sample size is usually in the range 200-500 μg, although on occasions glass fragments as small as 50 μg have been analyzed successfully. The sample is digested with 0.5 ml of the 1HF:2HCl acid mixture, and 0.5 ml Cr solution plus 0.5 ml B solution are added as internal standards, and the whole is diluted to 3.5 ml with deionized water. A typical sequential analysis covering Mn, Fe, Mg (two wavelengths), Al, Sr and Ba takes 3-4 minutes. Two Mg wavelengths are used in order to cover the wide variation in the concentration of this element that occurs in glass - from ppm levels in container glass to 2-3% in flat glass.

Within-run precisions for aqueous solutions, using the method as originally published (Catterick and Hickman 1979) are given in Table 3. Table 4 lists the short- and long-term precisions for the analysis of a typical flat glass, and Table 5 shows that real analyses - due to the low sample weights and the dilution factors involved - are often performed at only a few multiples of the ICP-AES detection limits.

It was recognized that a limitation of the method might be that the analytical response of the Cr internal standard (added to the sample solutions) was only examined during one forward and backward sequence per 3-4 min analysis. Continuous monitoring of an internal stan-

Table 3. ICP-AES ANALYSIS: WITHIN-RUN PRECISIONS USING AQUEOUS STANDARDS

Element	Mn	Fe	Mg	Al	Sr	Ba
Concentration	5.4 ppb	35.7 ppb	0.71 ppm	0.18 ppm	3.6 ppb	5.4 ppb
standard deviation (n=10)	12%	11%	10%	19%	15%	17%
Concentration	21.4 ppb	142.9 ppb	2.86 ppm	0.71 ppm	14.3 ppb	21.4 ppb
Relative standard deviation (n=10)	6%	4%	3%	9%	10%	9%

Table 4. ICP-AES ANALYSIS: SHORT- AND LONG-TERM PRECISIONS FOR THE ANALYSIS OF A TYPICAL FLAT GLASS, R.I. = 1.5171

Element	Mn	Fe	Mg	Al	Sr	Ba
Mean	85 ppb	0.071%	1.80%	0.51%	41 ppm	107 ppm
standard deviation (n=10, 1 day)	5%	15%	4%	8%	9%	8%
Relative standard deviation (n=10, 10 months)	11%	16%	8%	12%	12%	10%

Table 5. ICP-AES ANALYSIS: WORKING CLOSE TO THE DETECTION LIMIT

Element	Mn	Fe	Mg	Al	Sr	Ba
Wavelength/nm	257.6	259.9	278.0	396.1	407.8	455.4
Detection limit*	1.4 ppb	6.2 ppb	0.05 ppm	0.03 ppm	0.4 ppb	1.3 ppb
Multiples of detection detection limit in 3.5 ml solution from 200 - 500 µg fragments of glass	3 - 9	6 - 16	20 - 50	10 - 25	6 - 15	5 - 12

*Winge, R. K., Peterson, V. J. and Fassel, V. A. (1979) Applied Spec. 33:206-219

Table 6. THREE-MONTH PRECISIONS FOR THE ANALYSIS OF A STANDARD GLASS, WITH AND WITHOUT CONTINUOUS MONITORING OF AN INTERNAL STANDARD

200 - 500 µg fragments of a typical flat glass, ultrasonic nebulisation

Element	Mn	Fe	Mg	Al	Sr	Ba
Concentration in glass	83 ppm	0.069%	2.17%	0.52%	37 ppm	110 ppm
Without continuous monitoring of an internal standard (61 analyses)	11.4%	13.2%	7.8%	11.6%	10.8%	9.3%
With continuous monitoring of an internal standard (66 analyses)	8.3%	8.6%	5.9%	5.5%	7.1%	6.3%
Reduction in RSD:	27%	35%	24%	53%	34%	32%

dard was therefore investigated as a means of improving the analytical precision (Catterick 1984). A reference monochromator (0.3 m) is used with boron as internal standard and monitoring of the 249.7 nm. This has given improved analytical precision, shown by reductions in the RSDs observed for each element over 3-month periods (Table 6).

Although the ultrasonic nebulizer we employ has given good service for a number of years - and continues in regular use - it suffers from the limitation of not easily being automated. Consequently, other nebulizers have been evaluated as replacements. The main requirements for our purposes are low sample uptake rate and acid resistance - or alternatively treatment of the HF solutions with boric acid. We have found that a number of alternative nebulizers worked satisfactorily, with similar S/N levels and similar precisions for glass analysis. The S/B value of the homemade ultrasonic nebulizer was higher than more conventional nebulizers.

Whilst the ICP-AES instrument described is now somewhat out of date and our analytical scheme is limited in practice to a handful of elements, the availability of commercial instrumentation means that it is now relatively easy and inexpensive to determine 10 or 20 elements either simultaneously or rapid sequentially with ICP-AES systems. If computer reduction of data is involve, there is little extra effort on the part of the analyst compared to determining a couple of elements by AAS.

Uchida *et al.* (1979) employed ICP-AES for the determination of major and minor elements in silicates.

Locke (1980) and Carpenter (1985) have both reported the application and evaluation of the technique for some types of forensic material. More recently, Koons *et al.* (1988) employed ICP-AES to determine nine elements in glass samples for forensic purposes, and they examined their data using various pattern recognition techniques. Wolnik *et al.* (1989) also determined nine elements in small glass samples by ICP-AES, and utilized an HF resistant torch.

Atomic spectroscopy: direct current plasma - atomic emission spectrometry: Burdo and Snyder (1979) utilized direct current plasma - atomic emission spectrometry to determine boron in glass following dissolution in HF.

Atomic spectroscopy: inductively coupled plasma - mass spectrometry: Vandecasteele *et al.* (1989) have reported the use of ICP-MS in the analysis of high purity quartz sand.

SELECTION OF ELEMENTS FOR CLASSIFICATION AND DISCRIMINATION

Early work at the Metropolitan Police Forensic Science Laboratory led to a number of elements being recommended for classifying or discriminating glass samples. Blacklock *et al.* (1976), having quantitatively determined Al, Ba, Ca, Fe, Mg and Mn, found Mg, Fe and Mn to be especially useful for classifying sheet, container and tableware glasses, whilst Al was less useful than Ba for discriminating sheet glass. Due to its high correlation with RI, Ca was stated as being of no value for either classification of discrimination. Hughes *et al.* (1976) determined As, Fe, Cr, Mg, Mn, Na and Pb in eight samples of sheet, container and tableware glasses, and selected Mg and Mn as elements warranting further study for classification.

Based on this previous work, and taking due consideration of the experience of others as well as the capabilities of the technique, we selected the five elements Mn, Fe, Mg, Al and Ba when we were developing our ICP-AES procedure. This was a selection based on the primary requirement for classification; in practice the five-elements worked well for classification (Hickman 1981), and also provided a pleasing degree of discrimination. On occasions, when it is known that headlamp glass is to be analyzed, boron will be additionally determined.

Subsequently, a systematic study to establish the best elements for achieving good classification and discrimination in two areas of importance in forensic glass examination was carried out (Hickman *et al.* 1983):

1 — 18 flat, 16 container and 15 tableware glasses (all colorless) within the RI range 1.5177 - 1.5183 (where RI gives little indication of glass type) were selected for studying the problem of classification.

2 — 15 colorless flat glass samples of RI 1.5160 -1.5161 were chosen to investigate the discrimination of this type of glass.

Each group of glasses was analyzed for as many elements as was practical using NAA, ICP-AES, flame-AAS and flame-AES (Table 7). The sample size was not restricted to casework-sized fragments and reliable data for 22 elements were obtained for all samples.

The classification data were evaluated both by simple inspection and by stepwise discriminant analysis. For the test group of flat, container and tableware glasses the best classifying elements were found to be Mg, Li, Co, Sr, Fe and As. Magnesium separated all three types of glass from each other, Li was useful for separating sheet from tableware glasses and likewise Co for separating sheet from container glasses. A combination of these six best elements was found to perform some 85% of the separation produced by 22 elements. The elements of use for the various separations, in terms of distinguishing sheet, container and tableware glasses, are given in Table 8.

The discrimination data were evaluated simply by relating the sensitivity of the analytical technique employed to the range of values obtained for each element. Barium, Rb, Sr, Fe, K, Mn and Li were identified as good discriminatory elements. A summary of the findings is given in Table 9. A consequence of this work is

Table 7. ANALYSIS OF TEST GLASSES

Technique employed	Elements determined
ICP-AES	Mn Fe Mg Al Sr Ba
NAA	Na Cs Sc La Ce Eu Th Cr Se U Zn Ca
flame-AES	K Rb Li
AAS	As

Table 8. ELEMENTS FOR CLASSIFYING SHEET, CONTAINER AND TABLEWARE GLASS SAMPLES

Good for S / C / T separation	Good for S / C + T separation	Good for S / C separation	Good for S / T separation	Limited use for classification
Mg	As	Al	K Mn	Na Ca
	Fe	Co	Rb Cr	Ba Zn
	Sr		Li Th	Ce La
			Sc Cs	U Eu

Table 9. ELEMENTS FOR DISCRIMINATING SHEET GLASS SAMPLES OF REFRACTIVE INDEX 1.5160 - 1.5161

Good elements, likely to determine	Good elements, unlikely to determine
As Ba Rb Sr (Cr Zn)	Ce Co Cs La Na Sc Th U
Intermediate elements	Poor elements
Fe K Mn Li	Ca Mg Al Eu

the inclusion of Sr (which is determined with similar precision to Ba) in the ICP-AES procedure we use routinely for casework glass samples and it has proved to be a valuable discriminating element.

These selections of the best elements for classification and discrimination are of course a function of the samples selected and the sensitivities of measurement. Glass samples that are representative of U. K. usage are unlikely to form a representative sample of the types of glass encountered in other countries. If alternative analytical techniques, of different analytical sensitivity, were used then the selections of best elements might well be different. In addition, any improvement in the precision of analysis should lead to better discrimination.

DISCRIMINATION AND CLASSIFICATION USING ELEMENTAL DATA

Discrimination Test

A simple discrimination test is employed in casework comparisons of control and suspect glass analyses. Using the mean concentrations of the measured elements, the (mean ± 2 standard deviations) ranges of each of the elements determined are calculated for the two samples. These ranges are compared; if they overlap for every element the samples are reported as indistinguishable, whereas if the ranges for one or more elements are separate then the samples are reported as distinguishable. The standard deviations used in this test are those calculated from 240 analyses (mean sample weight = 270 μg) of a typical sheet glass performed during a ten-month period (Table 4).

By using the 10 month RSDs (which are larger than short-term RSDs), the discrimination test will err on the side of caution. A casework example of discrimination using in-run RSDs is given in Table 10.

This discrimination test is based on six elements, but it is likely that the test will increase in its power to discriminate with an increase in the number of variables.

Variation in Discrimination with RI

A study (Hickman 1983) of the variation in discriminating ability (of a six-element ICP-AES analysis) with RI for sheet glass samples is summarized by the plot given in Figure 4. Ten groups of glasses were selected as representative of narrow ranges of RI within the overall RI region 1.5150 - 1.5210; the number of glasses in each group varied from 13 to 30 samples.

Figure 4 shows that the discrimination provided by the six-element ICP-AES analytical scheme varies from 40% to over 90%, depending on the RI. Chemical analysis thus provides improved discriminating ability compared to the measurement of RI alone, although it is unfortunate that the best discrimination occurs in the wings of the RI distribution for sheet glasses (compare Figure 4 with Figure 1). Poor discrimination has been observed amongst glasses manufactured by the float

Table 10. A CASEWORK EXAMPLE OF THE DISCRIMINATION TEST

Two control samples of similar R.I. were each analyzed in triplicate, and the discrimination test was applied using the typical relative standard deviations:

Element	Mn	Fe	Mg	Al	Sr	Ba
Relative standard deviation	11%	16%	8%	12%	12%	10%

The ranges for all elements overlapped, and the samples would normally have been reported as indistinguishable.

However, when the within-run relative standard deviations from 10 replicates of control (A) and 12 replicates of control (B) were used, the samples were identified as distinguishable:

	Mn	Fe	Mg	Al	Sr	Ba
Relative (A) standard deviation	10.4%	11.0%	4.2%	6.9%	5.7%	10.0%
Relative (B) standard deviation	7.7%	4.0%	6.2%	10.4%	9.2	7.5%

	Fe range	Sr range	Ba range
(A)	0.059 - 0.093	34 - 42	89 - 133
(B)	0.103 - 0.121	58 - 84	132 - 178

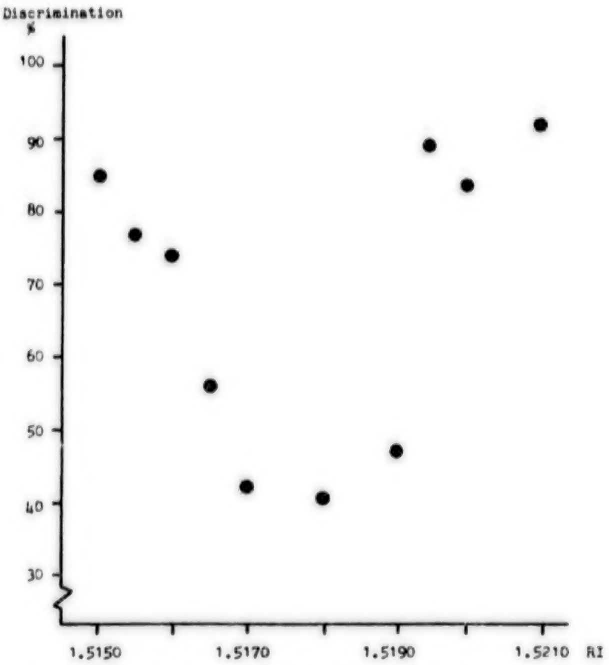


Figure 4. Variation in discriminating ability of a six-element ICP-AES analysis with refractive index.

glass process, especially glasses with RIs in the range 1.517 - 1.519.

Examination of the six-element data revealed that for glasses of RI below 1.519 most discriminations were based on one or two elements, whereas at higher RIs the glasses were more likely to be discriminated by four, five or six elements. The actual elements performing the discrimination appeared to vary with RI: Sr was a very good discriminator for glasses of RI < 1.5165 whilst Ba was useful at higher RIs. Manganese and Fe were also important but Mg and Al were found to be poor discriminating elements (cf. Table 9).

Classification

Classification is dependent on having a library of analyses with which to compare the analysis of an unknown sample. Our general approach to classifying glass samples is illustrated with a data set of glasses having refractive indices of approximately 1.5170. Seventy-eight glass samples in the background reference collection were identified as having RIs in the range 1.5168 - 1.5172: 67 flat, 3 tableware, 5 container and 3 headlamp. ICP-AES analysis of these produced a 78 sample x 7 variable data set (6 elements plus RI).

A number of approaches can be used to examining such a multi-sample, multi-variate data set. One such approach is cluster analysis, also known by other names such as Q-analysis, typology, grouping, clumping, numerical taxonomy and unsupervised pattern recognition - depending on the field to which the method is applied.

There are four main steps to a cluster analysis:

1 — select the variables (which should be continuous variables, for example, elemental concentration);
2 — construct the data matrix;
3 — measure the similarity between the samples;
4 — perform the cluster analysis.

After considerable trial and error we now employ a standard measure of similarity between samples: Squared Mean Euclidean Distances (SMEDs).

When SMEDs (using six elements plus RI) were calculated between the pairs of samples in the test set, and cluster analysis was performed, the dendrogram shown in Figure 5 was obtained. This shows that the tableware, container and headlamp glasses formed three separate clusters and were quite distinct from the flat (sheet) glasses. The application of standard discriminant analysis procedures to these data confirmed the complete separation of the four main groups (flat or sheet, tableware, container and headlamp).

The dendrogram of Figure 5 also showed a number of sub-groups within the flat or sheet category. Two glasses were grouped together, separate from the other samples; their Ba concentrations of 606 and 574 $\mu g.g^{-1}$ were significantly higher than the range (19 - 257 $\mu g.g^{-1}$) of the other sheet glasses. The dendrogram indicated that the remaining sheet glasses could be divided into four groups: of 30, 15, 14 and 6 samples. Discriminant analysis supported this supposition to some extent, but if the elemental ranges of the groups are compared (Table 11) it can be seen that, whilst all four groups can be separated, the only distinguishing feature between groups 1 and 2 is Fe concentration. In view of the known contamination problems in determining Fe, which lead to high coefficients of variation, it is felt that this difference on

Table 11. ELEMENTAL RANGES FOR FOUR GROUPS OF FLAT GLASS

Group	n	Mn/ppm	Fe/%	Mg/%	Al.%	Sr/ppm	Ba/ppm
1	30	5 - 93	0.049 - 0.076	1.6 - 2.4	0.40 - 0.62	31 - 56	77 - 121
2	15	64 - 101	0.075 - 0.130	1.6 - 2.3	0.48 - 0.77	35 - 51	97 - 142
3	14	40 - 97	0.061 - 0.111	2.0 - 2.5	0.48 - 0.74	75 - 201	105 - 257
4	6	21 - 85	0.039 - 0.059	2.0 - 2.6	0.32 - 0.71	33 - 56	19 - 85

Fe is marginal and it is better to consider these two groups as a single group of 45 glasses.

When discriminant analysis was applied to the main groups of 45, 14 and 6 samples, plus the 2 high-Ba sheet glass samples, very good separation of these four sheet glass groups was observed.

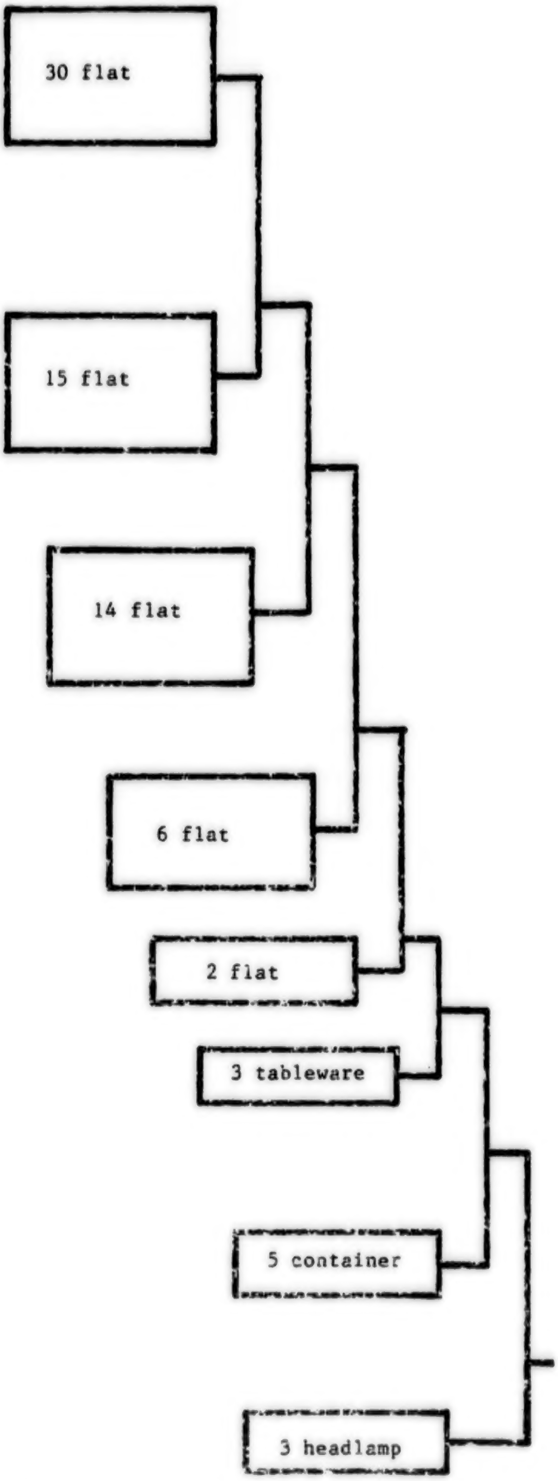


Figure 5. Dendrogram, based on six elements and refractive index, of 78 glasses of RI 1.5168 - 1.5172.

Identification of Groups of Glasses from Elemental Data

The problem of sample comparison increases when many samples are to be compared. One may end up with a tabulation of tens of variables and hundreds of samples. In a general sense such a data set should be examined to identify similar samples and also to see if such groupings of similar samples can be related to some other factor. For forensic purposes, we would like to classify glass samples as container, sheet, headlamp, etc.

A background reference collection of glass analyses by ICP-AES has been built up during the past four years and now comprises the five- or six-element analyses of more than 1350 glass samples (Table 12).

Various statistical procedures, including cluster analysis, have been applied to these background data in order to identify groups of samples similar in composition. These studies have shown that within the overall flat or sheet, container, headlamp, etc., divisions there occurred several different compositional types. At least 22 well-defined groups have been identified.

The requirement of classification rather than absolute characterization has resulted in some of these groups being large and quite diffuse: such groups may contain several compositional types. It has been possible to relate some of the groups to particular sources of manufacture, for example, float glass from Boussois, France, is characterized by a high level (>0.1%) of Ba, and float glass from Stolberg, Germany, has a distinctive (low) concentration of Al. The logical extension of these findings would be to assign all groupings of similar glasses to manufacturers' products or formulations, with the probable sub-division of the larger groups already identified.

A number of the samples in the background collection could not be assigned to the major groups. Some of these samples formed small groupings (<10 samples), either of a single class or of samples from two or more

Table 12. GLASS REFERENCE COLLECTION

1350 glasses analyzed by ICP-AES	
1350 samples	
895 flat (66.3%)	455 non-flat (33.7%)
660 window	145 container
225 vehicle	170 tableware
10 mirror	60 headlamp
	50 bulb
	8 lens
	22 miscellaneous

Table 13. CLASSIFICATION SCHEME FOR UNKNOWN GLASS SAMPLES

Distances sorted to find closest samples to unknown ten nearest neighbors to sample ABC/1:

SAMPLE	TYPE	DISTANCE	MN/PPM	FE/%	MG/%	AL/%	BA/PPM	R.I.
ABC/1		0.0000	15.00	0.020	0.075	0.37	181.0	1.5184
2668	T	0.00727	12.00	0.016	0.055	0.41	212.0	1.5184
774	S	0.03589	25.00	0.039	0.070	0.37	95.0	1.5246
2544	T	0.05070	17.00	0.015	0.160	0.68	385.0	1.5177
3151	C	0.06858	10.00	0.027	0.029	0.79	92.0	1.5197
1463	C	0.07848	13.00	0.025	0.023	0.78	91.0	1.5186
1703	C	0.08501	8.00	0.023	0.020	0.66	108.0	1.5183
1667	C	0.08823	29.00	0.033	0.294	0.61	173.0	1.5183
1411	C	0.08857	34.00	0.036	0.270	.055	171.0	1.5167
1684	C	0.09008	29.00	0.026	0.340	0.49	177.0	1.5173
2553	T	0.09110	14.00	0.013	0.240	0.56	61.0	1.5178

List of similar samples to sample ABC/1 - distances less than 0.0300:

2668	0.00727

classes. The most common class overlap was container with low Mg (that is, mostly pre-1930 production) sheet glass. Some glasses in the collection are of essentially unique composition and these are all unusual samples, for example, a yellow drinking glass, a green ornament and a black sheet glass.

Classification Scheme

Since the elemental ranges of these groups are, to a large extent, mutually exclusive they can be used to classify glass samples.

Table 14. CLASSIFICATION SCHEME FOR GLASS SAMPLES ANALYZED BY ICP-AES

258 trial samples, 3-year period			
Definite classification	–	correct	190 (73.6%)
	–	incorrect	0
Single suggestion	–	correct	32
	–	incorrect	0
Double suggestion	–	correct	17
	–	incorrect	0
Unclassible			19 (7.4%)
620 casework samples, 8-year period			
Definite classification	–	correct	453 (73.1%)
	–	incorrect	0
Single Suggestion	–	correct	72
	–	incorrect	2
Double suggestion	–	correct	15
	–	incorrect	0
Unclassifiable			78 (12.6%)

On the simplest level a direct comparison of a 6-element analysis with the ranges of the 22 groups can provide a classification.

We employ computer-based comparisons of an unknown's analysis with separate sets of data for flat and non-flat glasses, giving print-outs of the ten nearest samples to the unknown (for example, the non-flat comparison of Table 13). Examination of the nearest neighbors produces either definite classifications or suggestions - of single or multiple types of glass. In casework this procedure has produced a very high rate of successful classifications (Table 14).

Casework Examples

Broken glass from the laminated side window of a Mercedes car was analyzed, and this revealed that the two sheets were distinguishable chemically (Table 15). The presence of both types of glass on a suspect's clothing would provide important evidence.

The data shown in Table 16 refer to the analysis of the broken side windows from four automobiles parked in one street. The four samples are quite distinct, both in terms of RI and chemical composition. Over 300 fragments of glass were recovered from the surface and pockets of a suspect's jacket. These represented at least ten different sources of glass, and included fragments that matched the control samples.

A case involving the deliberate contamination of jars of baby food with fragments of glass produced a great many casework submissions for analysis. A selection of the results is given in Table 17, along with the results of applying our classification scheme to these data. It was important to be able to distinguish the recovered fragments from the glass of the containers, and

Table 15. ICP-AES ANALYSIS OF THE LAMINATED SIDE WINDOW FROM A MERCEDES AUTOMOBILE

R.I. of side 1 glass = 1.5207, R.I. of side 2 glass = 1.5217

Mean of triplicate analyses

	Mn/ppm	Fe/%	Mg/%	Al/%	Sr/ppm	Ba/ppm
side 1	56	0.40	1.82	0.33	83	75
side 2	70	0.061	1.82	0.28	82	67

Two sheets of the laminate are distinguishable by Fe content.

The samples were not classifiable by comparison with the 1350 sample reference collection.

Table 16. ICP-AES ANALYSIS OF SAMPLES FROM THE SIDE WINDOWS OF FOUR AUTOMOBILES

Mean of triplicate analyses

	Mn/ppm	Fe/%	Mg/%	Al/%	Sr/ppm	Ba/ppm	R.I.
Sample (A)	46	0.33	2.40	0.70	47	67	1.5231
Sample (B)	20	0.071	2.28	0.12	42	15	1.5178
Sample (C)	36	0.16	2.28	0.85	43	119	1.5147
Sample (D)	58	0.046	2.43	0.21	75	42	1.5210

Table 17. ICP-AES ANALYSIS OF GLASS FRAGMENTS RECOVERED FROM VARIOUS SAMPLES OF BABY FOOD

Mean of triplicate analyses

	Mn/ppm	Fe/%	Mg/%	Al/%	Sr/ppm	Ba/ppm	R.I.	Class
Sample (A)	<20	0.029	1.31	0.71	58	350	1.5141	T
Sample (B)	<20	0.027	0.57	0.74	227	175	1.5184	T
Sample (C)	95	0.085	1.65	0.61	132	162	1.5191	F
Sample (D)	138	0.047	0.22	0.74	186	477	1.5194	U
Sample (E)	220	0.028	0.24	0.71	144	160	1.5206	C
Sample (F)	228	0.026	0.25	0.69	139	158	1.5206	C
Sample (G)	102	0.053	0.78	0.59	118	147	1.5207	U
Sample (H)	95	0.062	0.86	0.63	123	169	1.5209	U
Sample (I)	102	0.057	0.71	0.61	127	157	1.5209	U
Sample (J)	91	0.055	0.75	0.60	123	155	1.5210	U
Sample (K)	60	0.242	0.31	0.37	119	65	1.5313	F
Sample (L)	<20	0.061	0.03	0.96	88	290	1.5362	U
Sample (M)	<20	0.052	0.02	0.90	79	259	1.5362	U

analysis by ICP-AES provided this. It was also possible to observe related instances of tampering, together with a number of copycat crimes.

REFERENCES

Blacklock, E. C., Rogers, A., Wall, C. and Wheals, B. B. (1976). The quantitative analysis of glass by emission spectrography: A six element survey, Foren. Sci. 7:121-130.

Bradford, L. W. and Devaney, J. (1970). Scanning electron microscopy applications in criminalistics, J. Forens. Sci. 15:110-119.

Burdo, R. A. and Wise, W. M. (1975). Determination of silicon in glasses and minerals by atomic absorption spectrometry, Anal. Chem. 47:2360-2364.

Burdo, R. A. and Snyder, M. L. (1979). Determination of boron in glass by direct current plasma emission spectrometry, Anal. Chem. 51:1502-1508.

Butterworth, A. (1974). The laser microspectral analyzer, J. Foren. Sci. Soc. 14:123-129.

Butterworth, A., German, B., Morgans, D. and Scaplehorn, A. (1974). A report on an investigation into the trace elements present in vehicle headlamp and auxiliary lamp glasses, J. Foren. Sci. Soc. 14:41-45.

Carpenter, R. C. (1985). The analysis of some evidential materials by inductively coupled plasma - optical emission spectrometry, Foren. Sci. Int. 27:157-163.

Catterick, T. (1984). Continuous internal standardisation with a sequential inductively coupled argon plasma system, Analyst 109:1465-1467.

Catterick, T. and Hickman, D. A. (1979). Sequential multi-element analysis of small fragments of glass by atomic-emission spectrometry using an inductively coupled radiofrequency argon plasma source, Analyst 104:516-524.

Catterick, T. and Wall, C. D. (1978). Rapid analysis of small glass fragments by atomic absorption spectroscopy, Talanta 25:573-577.

Cerlon, P. (1958). Quantitative spectrographic analysis in criminalistics, J. Foren. Sci. 3:109-115.

Coleman, R. F. and Goode, G. C. (1973). Comparison of glass fragments by neutron activation analysis, J. Radioanal. Chem. 15:367-388.

Coleman, R. F. and Weston, N. T. (1968). A case concerning neutron activation analysis of glass, J. Foren. Sci. 8:32-33.

Coleman, R. F. and Wood, G. A. (1968). The value of trace analysis in the comparison of glass fragments - a preliminary study, Atomic Weapons Research Establishment Report 03/68 (17pp).

Cregeen, W. A. (1960). The spectrographic examination of small samples by a procedure giving high sensitivity, J. Foren. Sci. 5:226-235.

Dabbs, M. D. G., German, B., Pearson, E. F. and Scaplehorn, A. W. (1973). The use of spark source mass spectrometry for the analysis of glass fragments encountered in forensic applications, Part II, J. Foren. Sci. Soc. 13:281-286.

Fuller, C. W. and Whitehead, J. (1974). The determination of trace metals in high-purity sodium calcium silicate glass, sodium borosilicate glass, sodium carbonate and calcium carbonate by flameless atomic absorption spectrometry, Anal. Chim. Acta 68:407-413.

German, B., Morgans, D., Butterworth, A. and Scaplehorn, A. (1978). A survey of British container glass using spark source mass spectrometry with electrical detection, J. Foren. Sci. Soc. 18:113-121.

German, B. and Scaplehorn, A. W. (1972). The use of spark source mass spectrometry for the analysis of glass, J. Foren. Sci. Soc. 12:367-374.

Goode, G. C., Baker, C. W. and Brooke, N. M. (1969). An automated solvent-extraction technique for radiochemical group separations: application to the analysis of glass fragments by thermal-neutron activation, Analyst 94:728-736.

Goodwin, D. G., Hamer, P. S., Hayes, P. M. and Underhill, M. (1985). The microscopic examination of glass surfaces, J. Foren. Sci. Soc. 25:459-469.

Haney, M. A. (1977). Comparison of window glasses by isotope dilution spark source mass spectrometry, J. Foren. Sci. 22:534-543.

Harrison, P. H., Lambert, J. A. and Zoro, J. A. (1985). A survey of glass fragments recovered from clothing of persons suspected of involvement in crime, Foren. Sci. Int. 27:171-187.

Harvey, C. E. (1968). Emission spectrochemical analysis of submilligram samples, J. Foren. Sci. 13:269-278.

Headridge, J. B. and Riddington, I. M. (1984). Determination of silver, lead and bismuth in glasses by atomic absorption spectrometry with introduction of solid samples into furnaces, Analyst 109:113-118.

Hickman, D. A. (1981). A classification scheme for glass, Foren. Sci. Int. 17:265-281.

Hickman, D. A. (1983). Elemental analysis and the discrimination of sheet glass samples, Foren. Sci. Int. 23:213-223.

Hickman, D. A., Harbottle, G. and Sayre, E. V. (1983). The selection of the best elemental variables for the classification of glass samples, Foren. Sci. Int. 23:189-212.

Hoare, H. C., Mostyn, R. A. and Newland, B. T. N. (1968). An ultrasonic nebulizer applied to atomic absorption spectrophotometry, Anal. Chim. Acta 40:181-186.

Howden, C. R., German, B. and Smalldon, K. W. (1977). The determination of iron and magnesium in small glass fragments using flameless atomic absorption spectrophotometry, J. Foren. Sci. Soc. 17:153-159.

Howden, C. R., Dudley, R. J. and Smalldon, K. W. (1978). The analysis of small glass fragments using energy dispersive X-ray fluorescence spectrometry, J. Foren. Sci. Soc. 18:99-112.

Hughes, J. C., Catterick, T. and Southeard, G. (1976). The quantitative analysis of glass by atomic absorption spectroscopy, Foren. Sci. 8:217-227.

Jones, A. H. (1965). Analysis of glass and ceramic frit by atomic absorption spectrophotometry, Anal. Chem. 37:1761-1762.

Keeley, R. H. and Christofides, S. (1979). Classification of small glass fragments by X-ray microanalysis with the SEM and a small sample XRF spectrometer, Scanning Electron Microscopy I:459-464.

Kilroy, W. P. and Moynihan, C. T. (1978). Atomic absorption analysis of glass, Ceram. Bull. 57:1034-1035.

Koons, R. D., Fiedler, C. and Rawalt, R. C. (1988). Classification and discrimination of sheet and container glasses by inductively coupled plasma - atomic emission spectrometry and pattern recognition, J Foren. Sci. 33:49-67.

Korda, E. J., Pruden, L. H. and Williams, J. P. (1973). Elemental analysis of glass and glass ceramics with the scanning electron microscope, Amer. Ceramic Soc. Bull. 52:279.

Locke, J. (1980). The application of plasma source atomic emission spectrometry in forensic science, Anal. Chim. Acta 113:3-12.

Locke, J., Boase, D. and Smalldon, K. W. (1978). The use of spark source mass spectrometry for the analysis and classification of small glass fragments, J. Foren. Sci. Soc. 18:123-131.

Maehly, A. and Stromberg, L. (1981). Chemical Criminalistics, Springer-Verlag, pp. 155-169.

Marcouiller, J. M. (1990). A revised glass annealing method to distinguish glass types, J. Foren. Sci. 35:554-559.

Pearson, E. F., May, R. W. and Dabbs, M. D. G. (1971). Glass and paint fragments found in men's outer clothing - report of a survey, J. Foren. Sci. 16:283-300.

Perkons, A. K. and Jervis, R. E. (1962). Applications of radio-activation analysis in forensic investigations, J. Foren. Sci. 7:449-464.

Pounds, C. A. and Smalldon, K. W. (1978). The distribution of glass fragments in front of a broken window and the transfer of fragments to individuals standing nearby, J. Foren. Sci. Soc. 18:197-203.

Reeve, V., Mathiesen, J. and Fong, W. (1976). Elemental analysis by energy dispersive X-ray: a significant factor in the forensic analysis of glass, J. Foren. Sci. 21:291-306.

Ruch, R. R., Buchanan, J. D., Guinn, [illegible] lanca, S. C. and Pinker, R. H. (19[illegible] ctivation analysis in scientific crime [illegible] recent developments, J. Foren. Sci. 9:119-13[illegible].

Schmitt, R. A. and Smith, V. (1970). Identification of origin of glass by neutron activation analysis in a forensic case, J. Foren. Sci. 15:252-260.

Smale, D. (1973). The examination of paint flakes, glass and soil for forensic purposes, with special reference to electron probe microanalysis, J. Foren. Sci. Soc. 13:5-15.

Uchida, H., Uchida, T. and Iida, C. (1979). Determination of major and minor elements in silicates by inductively coupled plasma emission spectrometry, Anal. Chim. Acta 108:87-92.

Vandecasteele, C., Wauters, G., Dams, R. and de Jonghe, W. (1989). Analysis of high purity quartz sand by inductively coupled plasma mass spectrometry, J. Analyt. At. Spectrom. 4:461-463.

Vasan, V. S., Stewart, W. D., Jr. and Wagner, J. B., Jr. (1973). X-ray analysis of forensic samples using a scanning electron microscope, J. Assoc. Off. Analyt. Chem. 56:1206.

Walls, H. J. (1968). Forensic Science, Sweet & Maxwell Ltd., London, p. 22.

Walsh, K. A. J. and Buckleton, J. S. (1986). On the problem of assessing the evidential value of glass fragments embedded in footwear, J. Foren. Sci. Soc. 26:55-60.

Welch, A., Richard, R. and Underhill, M. (1989). The observation of banding in glass fragments and its forensic significance, J. Foren. Sci. Soc. 29:5-13.

Whitney, W. P. and MacDonell, H. L. (1964). Forensic applications of the electron microprobe, J. Foren. Sci. 9:511-519.

Wise, W. M. and Solsky, S. D. (1977). Determination of aluminium in glass by atomic absorption spectroscopy, Anal. Lett. 10:273-282.

Wolnik, K. L., Gaston, C. M. and Fricke, F. L. (1989). Analysis of glass in product tampering investigations by inductively coupled plasma atomic emission spectrometry with a hydrofluoric acid resistant torch, J. Analyt. Atom. Spectrom. 4:27-31.

Zoro, J. A. (1983). Observations on the backward fragmentation of float glass, Foren. Sci. Int. 22:213-219.

THE APPLICATION OF ICP-ES AND ICP-MS TO THE INVESTIGATION OF PRODUCT TAMPERING

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According to Webster's Dictionary, the definition of tampering is "to alter for an improper purpose or in an improper way." Motives for product tampering include the intent to harm a specific person, the intent to injure the manufacturer of the product, the hope of obtaining compensation for alleged injuries, the desire for attention, and so on. Throughout history, as long as there have been commercially produced food and drug products, there have been instances of product tampering. However, in 1982 when seven unsuspecting consumers in the Chicago area died from taking Tylenol® that had been poisoned with cyanide (potassium cyanide), the random and wanton nature of the crime made the threat of consumer product tampering a nationwide concern. The Chicago Tylenol incident became one of the most widely publicized stories ever reported and polls at the time estimated 98% of the public had heard or read about the tragedy (Swanson 1986).

Food and Drug Administration (FDA) personnel manually examined millions of capsules from across the nation in an attempt to verify the extent of the tampering. No poisoned product was found outside the greater Chicago area. However, a bottle of Tylenol containing poisoned capsules was recovered from a suburban Chicago store by FDA investigators and two additional adulterated bottles were subsequently recovered in a Chicago area recall of Tylenol capsules. In total, eight bottles of Tylenol capsules were known to have been adulterated. Poisoned capsules from five adulterated bottles had caused seven deaths, three in one family. Authorities questioned whether all the poisoned products were directly related or whether some adulterated samples might be copy-cat incidents. From the perspective of the FDA, it was also important to rule out any cyanide found at the manufacturing site as an accidental or intentional source of poison in the product.

The identity and relative amounts of various elemental constituents in suspect samples such as glass or paint have been commonly used to identify and link or differentiate samples. In the Tylenol tampering incident, results of the determination of trace element contaminants in potassium cyanide (KCN) by inductively coupled plasma emission spectroscopy (ICP-ES) were used for making comparisons (Wolnik *et al.* 1984). Figure 1 illustrates results for samples of KCN collected at the manufacturing sites and from a Chicago warehouse where the product had been stored prior to distribution. Although the identity of the elemental contaminants did not vary, the relative amounts of these contaminants in various lots of KCN were representative and could be used to demonstrate similarities or differences between suspect samples. Note that the range indicated by the error bars in Figure 1 represents the range of results for analyses of KCN from adulterated capsules in the bottle recovered by FDA. Once Illinois Department of Law Enforcement authorities were convinced the technique had merit, portions of the remaining KCN from poisoned capsules linked to homicides were analyzed. Figure 2 illustrates comparison of results for KCN taken from capsules related to two homicides. Again, the range indicated by the error bars in Figure 2 represents the range of results of analyses of KCN from adulterated capsules in the bottle recovered by FDA. Note that in these homicide cases, KCN was removed from the capsules initially by examiners who could not foresee the potential significance of trace element contaminants. The apparent discrepancy for the sodium results emphasizes the necessity of trace element contamination control during every phase of sampling and analysis. Table 1 lists analytical results for KCN from different bottles of adulterated Tylenol and one homicide. In these instances, all samples were removed from the capsules in our laboratory using stringent contamination control techniques which include acid washed labware and the exclusive use of distilled deionized water with a metered resistance of 18 megohm/cm for thorough rinsing of labware and for making dilutions.

ICP-ES

Inductively coupled plasma emission spectrometry (ICP-ES) has a number of features which make it particularly well suited for determination of trace elements in materials such as potassium cyanide. Coupled with a polychromator, the ICP enables simultaneous multielement analysis of solutions with ppb detection limits for many elements, a linear range of 4 to 5 orders of magnitude for most elements and an unusual degree of freedom from matrix interferences that may cause signal suppression or enhancement. Corrections for back-

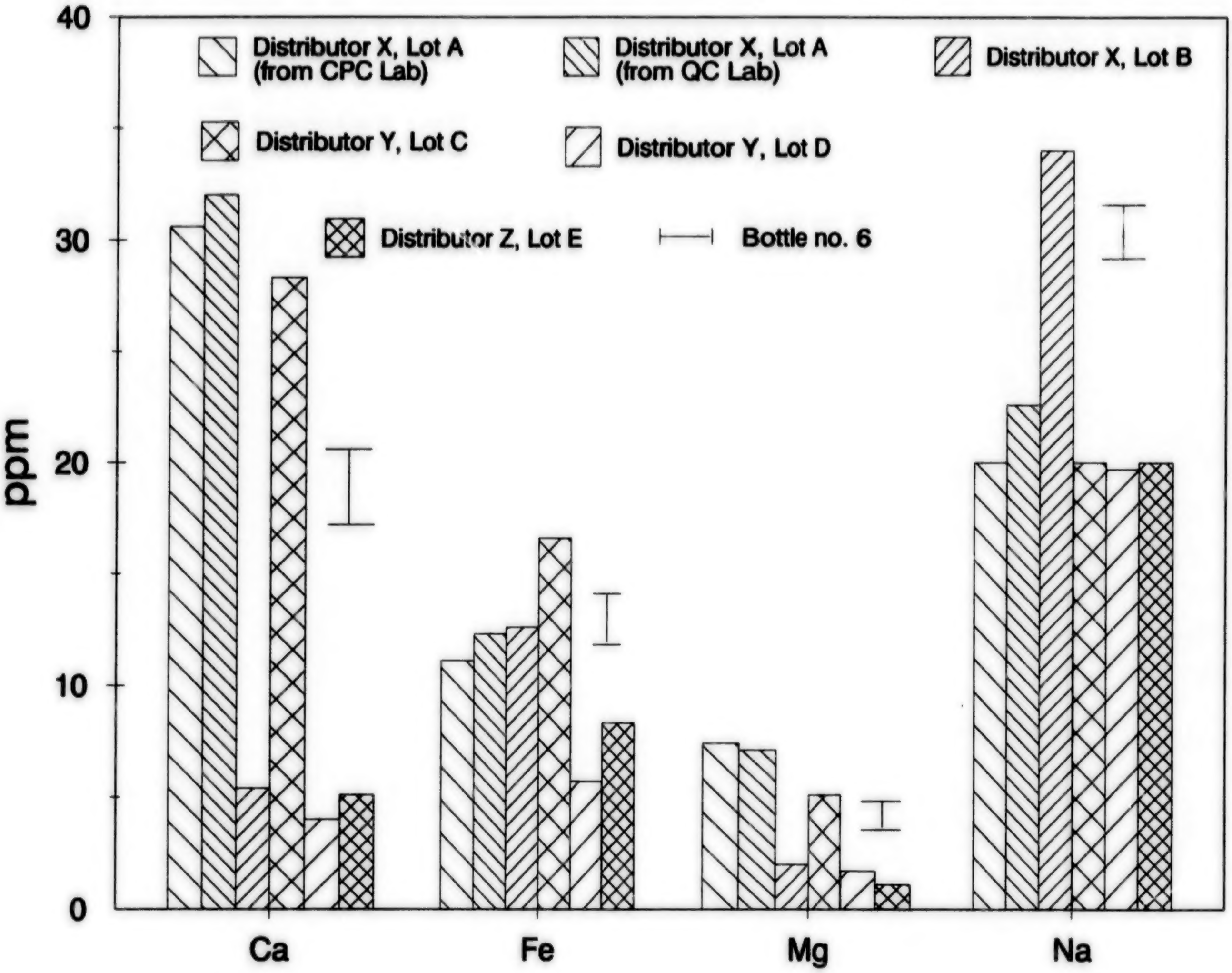

Figure 1. Results of analyses of KCN reagent samples and KCN from contaminated Tylenol capsules.

ground and spectral interferences can be made automatically. These attributes enable reliable, highly precise determinations of major and trace elements in a variety of samples with minimal sample pretreatment. The main drawback of the technique is that it is destructive, samples must be in solution (usually aqueous) and a minimum of 0.5 ml of solution is needed for analysis. In general, ICP scanning spectrometers require more sample per analysis than ICP polychromators. Samples with a high dissolved solids content can cause sample introduction problems. The severity of the problem depends on the nature of the matrix but in general it is best to limit dissolved solids to less than 1%. For the determination of trace elements in sodium or potassium cyanide, samples ranging in size from 10 mg to 1 g were diluted with distilled deionized water to a final concentration of 5 mg/ml (0.5%). A comprehensive treatment of inductively coupled plasma spectrometry can be found in the text by Montaser and Golightly (1987).

FATA

On October 13, 1983, The Federal Anti-Tampering Act (FATA) became law. This law mandates substantial fines and imprisonment for persons who knowingly place others at risk of injury or death by tampering with a product, product labeling or product container. In cases of actual injury or death, sentences from 20 years to life imprisonment can be imposed. The Anti-Tampering Act also mandates stiff penalties for tampering with intent to cause injury to a business and for false reports of tampering. See Appendix I. The U. S. Food and Drug Administration is responsible for investigating suspected tampering of drugs and most food products, often working in conjunction with other federal and local law enforcement agencies. Other regulations passed at approximately the same time required tamper-evident packaging for over the counter drug products. In the wake of several deaths in 1986 due to tampering with products in

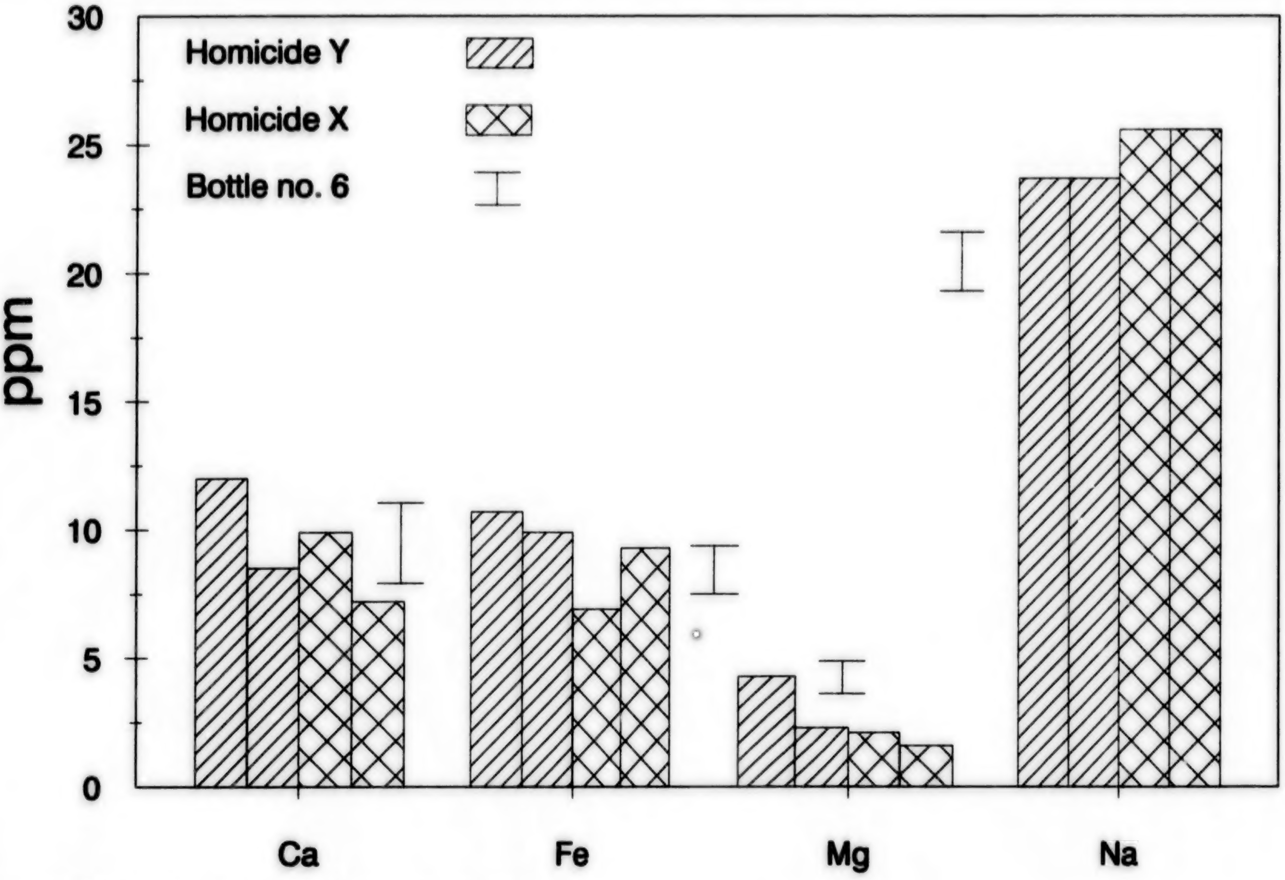

Figure 2. Results of analyses of KCN from contaminated capsules.

capsule form, many manufacturers discontinued the sale of over the counter drug products in the traditional two piece capsule. From 1975 to 1982 there were eight known deaths attributable to product tampering. From 1983 to the Spring of 1991 there have been eight additional deaths attributed to product tampering this would seem to indicate that packaging alone cannot deter the determined tamperer. There have been 28 convictions related to the Federal Anti-Tampering Act. Psychopathic killers, pranksters, the disgruntled and the greedy have been guilty of product tampering and false reports of tampering.

APPLICATIONS

Since 1982, our laboratory (formerly the FDA Elemental Analysis Research Center and currently the FDA National Forensic Chemistry Center) has used trace element determination by ICP-ES to assist in the investigations of 21 deaths and numerous alleged injuries associated with possible or confirmed product tampering with cyanide. The elements that were detected in most cyanides are Ca, Mg, Fe, and Na. Elements that have been found periodically are Si, Ba, Zn, Sr, and Cu. On occasion Ag and Cr have been detected. In many cases, the poisoned products were capsules but in some instances, foods such as instant soup mix, yogurt, or cola had been

Table 1. ELEMENTAL ANALYSIS OF KCN IN TYLENOL CAPSULES

Capsule	Ca (μg/g)	Fe (μg/g)	Mg (μg/g)	Na (μg/g)
1[a]	7.8	8.0	3.3	825
	8.6	8.6	3.5	940
2[a]	9.0	7.8	3.2	860
	10.9	8.0	3.7	800
	8.7	9.0	3.3	890
3[a]	8.3	8.4	3.4	870
	9.8	9.3	3.4	860
4[b]	9.6	9.7	3.5	1050
5[b]	9.1	8.3	3.3	940
	8.6	8.1	3.4	950
6[b]	9.2	8.9	3.4	1000
7[c]	7.7	7.4	3.4	960
	8.1	7.9	4.4	1200
	10.1	9.3	3.7	1050
8[d]	8.9	8.8	3.9	960
9[d]	8.8	9.0	3.7	840
Avg.	9.0	8.5	3.5	940
S.D.	±0.8	±0.6	±0.3	±100
% RSD	8.9	7.1	8.6	11.0

[a] Sixth bottle
[b] Seventh bottle
[c] Eighth bottle
[d] Homicide case (12 year old girl)

adulterated. Several deaths, in which capsules containing cyanide were found at the scene, were eventually ruled suicides, based in part on the fact that the victim had access to cyanide (either potassium or sodium) with a pattern of trace element contamination that matched the remaining poisoned product. Our most recent involvement in the investigation of product tampering homicide deals with two deaths in the Seattle area caused by Sudafed® capsules poisoned with cyanide.

In what might have been a related case, a 30-year-old man living near Seattle made an emergency call reporting that he was violently ill and had taken a Sudafed capsule. The man subsequently died while being treated at a local hospital. The death was attributed to cyanide poisoning. No Sudafed capsules were found among the victim's possessions or in a search of his home. The victim was employed by a company that manufactures printed circuit boards and as a consequence he had access to gold electrolyte plating solutions which contained cyanide as potassium dicyanoaurate. Our laboratory was asked to analyze samples of the victim's vomit for the presence of gold. During the initial analysis, a trace of antimony was detected in addition to 40 ppm gold. Analysis of the plating solution which was the most readily available to the victim also showed the presence of ppm levels of antimony as well approximately 5% gold. Based on our previous analyses of thousands of different food samples, neither gold nor antimony would be expected to be present in the stomach. This evidence, in addition to other incidents of attempted and threatened suicide by the victim, confirmed the opinion of the local authorities that this death should be attributed to self-induced cyanide poisoning rather than product tampering.

Cyanide is not the only toxic or hazardous substance used for product tampering. Caustic and corrosive chemicals seem to be popular choices for the tamperer, particularly in products such as eye wash or mouth wash. An interesting example of tampering involving a caustic substance occurred in 1986. A woman was admitted to a Dayton hospital with severe burning pains in her stomach that developed after she had taken a Benadryl® capsule. The capsules were packaged in a bubble type pack with a clear plastic over lay and a foil back. The attending physician noticed that one of the remaining capsules looked different from the others. Here moved the capsule from the packet, opened it, placed part of the contents on his tongue, and immediately experienced a burning sensation. The pH was confirmed as basic with indicator paper. A portion of the remaining capsule contents was delivered to the FDA for trace element characterization. We received only a few granules of material that had already adsorbed considerable moisture. Microscopic examination of the sample revealed what appeared to be three types of material, spheres, one metallic-like fragment and irregular granules we described as chunks. All appeared wet. Fortunately due to our experience with other product tampering investigations, we had authentic samples of several different drain cleaners on hand. Microscopic examination of authentic Crystal Drano® showed that it was composed of spheres, metallic fragments, irregular shaped crystals and flat, plate-like crystals. The appearance of other drain cleaners did not resemble the suspect material. Analysis of the spheres and chunks by ICP-ES did not provide useful elemental patterns; however, the metal fragment was aluminum and contained a number of elemental contaminants. Since we could not obtain an accurate weight for the metal fragment from the capsule, results for Cu/Al, Fe/Al, Mn/Al, and Zn/Al ratios to provide a basis for comparison to possible sources of the contamination. An opened can of Drano was recovered from the victim's home. Analysis of Al fragments from this can and other cans of Drano with the same lot number collected later showed similar Cu, Fe, Mn, and Zn ratios to the fragment from the contaminated Benadryl capsule. Aluminum fragments from four other lots of Drano collected by FDA investigators all had different trace element patterns. See Table 2 for a comparison of Cu, Fe, Zn and Mn to Al ratios for different lots of Drano. Subsequent to media publicity about the incident which indicated the family might be suspect, the victim became uncooperative with investigators. The case re-

Table 2. ICP SIGNAL RATIOS FOR Al FRAGMENTS IN DRANO

	Cu/Al x10	Fe/Al x100	Zn/Al x100	Ma/Al x1000
Drano - Lot A* from Residence	2.1	1.1	1.2	1.1
	2.3	1.1	1.3	1.1
	2.2	1.1	1.1	1.1
Drano 1 - Lot A	2.3	1.0	1.0	0.9
Drano 2 - Lot A	2.3	1.0	1.0	1.0
Drano 3 - Lot A	2.4	1.0	1.1	1.0
Drano 4 - Lot A	2.3	1.0	1.0	1.0
Drano - Lot B	2.1	1.0	1.2	0.2
Drano - Lot C	3.3	1.4	2.8	0.5
Drano - Lot D	2.1	1.0	1.9	0.2
Drano - Lot F	2.9	1.1	1.1	0.9

* 3 different fragments, analyzed at different times.

mains unresolved although there was strong evidence that the source of the tampering was Drano of the same lot found in the victim's home.

In 1986 following the death of a young woman in New York and two deaths in the Seattle area attributed to tampering, the FDA was plagued by an epidemic of reported tamperings. Numerous food and drug products were involved in thousands of cases of suspected tampering investigated by FDA during the summer of that year. A widely publicized report of glass found in baby food quickly led to extensive complaints of alleged tampering with this sensitive product. Using a modification (Wolnik *et al.* 1989) of procedures developed in the United Kingdom (Catterick and Hickman 1979,1981; Locke 1980; Hickman 1984) for the determination of the elemental composition of glass by ICP-ES, over 100 fragments were analyzed for comparison to the containers in which they were allegedly found. Glass from the container should represent other containers in process at the same time as the suspect product and which might,therefore, be a possible source of glass fragments introduced by manufacturing mishap. In the majority of cases analyzed in our lab, the contaminant fragments were not container glass (soda, lime, silica glass) but tumbler glass (soda, mixed calcite-dolomite, silica glass). Fragments analyzed ranged in size from a 200 μg fragment allegedly found in a baby's diaper to gram size pieces of glass that were so large they had to be correctly oriented to fit inside the baby food jar. Results of these analysis coupled with extensive investigational evidence demonstrated to the public that there were no widespread problems in the manufacture of baby food and quickly restored confidence in this important segment of the food supply.

ICP-MS

Another technique that has proven to be a useful tool for trace element analysis for investigation of product tampering is inductively coupled mass spectrometry (ICP-MS). In ICP-MS, singly charged analyte ions generated in the plasma are extracted into and measured with a quadrupole mass spectrometer. A chapter of the text by Montaser and Golightly (Horlick *et al.* 1987) is devoted to a discussion of the ICP-MS technique. Sub ppb detection limits (in the range of 10-100 pg/ml) are obtainable for most elements in dilute aqueous-acid solutions. Nearly every element in the periodic table can be determined by this technique. In addition to sensitivity and multielement capability, ICP-MS provides elemental isotope information which allows determination of natural isotope abundance patterns. These patterns serve as essentially immutable evidence for the qualitative identification of an element. Also, isotope dilution techniques can be used to solve and study analytical problems. When coupled with chromatography, the sensitivity of ICP-MS enables determination of elemental species (that is, valence state and associated organic moiety, etc.) at useful levels in a variety of sample types. However, the ICP-MS technique is not totally free of interferences and requires some sample preparation and careful quality control in order to obtain useful information from an analysis. Although elemental mass spectra are considerably simpler than optical emission spectra, molecular ions formed in the plasma or ion extraction device can cause interferences. In addition to causing spectral features, the sample matrix may induce changes, usually suppression, in the signal intensity. These effects are significant and often seriously degrade detection limits for trace elements in real samples. Dilution of the sample can reduce these effects but of course dilution worsens sample detection levels. However, even if the sample matrix precludes taking full advantage of the remarkable sensitivity of ICP-MS, a major benefit of the technique for forensic applications in product tampering is the ability to examine such a wide array of possible elements, rapidly with relatively low sample consumption.

A case in which ICP-MS proved particularly useful occurred in 1988 in the state of Oregon. A middle-aged man, diagnosed as suffering from arsenic poisoning, was treated and released from the hospital; however, he became ill again and was again diagnosed as suffering from arsenic poisoning. The local police naturally became suspicious and his wife was the prime suspect. A search of the couple's residence disclosed a bag of sugar with suspicious looking clumps of sugar granules. Analysis revealed the presence of arsenic in the sugar. Terro brand ant killer was suspected as the source of the arsenic. Our laboratory was asked to see if there was a link between the arsenic contaminated sugar and a bottle of Terro ant poison they forwarded to us. The bottle was labeled as containing sodium arsenate. Analysis by ICP-ES confirmed the presence of arsenic and sodium in the sugar. Neither element was detected in control sugar or unclumped sugar from the suspect bag. A combination of ion pair high performance liquid chromatography with post column hydride formation and determination of arsine by ICP-MS was used to determine the valence state of the arsenic in the clumped sugar. Since arsine is a gaseous species, the arsenic was effectively separated from the sample matrix by chromatography and from the column effluent by hydride formation. Arsenic was monitored as a function of time with As(III) having a retention time of 3 minutes and As(V) a retention time of 15 minutes. Arsenic (III) is the more toxic species but the As in the sugar was almost entirely As(V). During this procedure, relatively high levels of antimony were also detected in the clumped sugar. Isotope ratios of Sb^{121}

and Sb^{123} confirmed the presence of antimony. Subsequent determination of As and Sb in the clumped sugar and ant poison by graphite furnace atomic absorption and comparison of the Sb/As ratios provided the sought after link. The Sb/As ratio for the clumped sugar was 0.0340 and for the ant poison, 0.0301. A bottle of Terro® brand ant poison purchased in Cincinnati gave an Sb/As ratio of 0.0176.

CONCLUSION

In conclusion, trace element analysis (and sometimes speciation) by ICP-ES and ICP-MS is an important tool for the investigation of incidents of suspected or actual product tampering. The technique has also been used successfully to aid in the investigation of other criminal activities such as the counterfeiting of prescription drugs, the illegal sale of drugs such as anabolic steroids, smuggling, and generic drug fraud.

REFERENCES

Catterick, T. and Hickman, D. A. (1979). Sequential multi-element analysis of small fragments of glass by atomic-emission spectrometry using an inductively coupled radio frequency argon plasma source, Analyst 104:516-524.

Catterick, T. and Hickman, D. A. (1981). The quantitative analysis of glass by inductively coupled plasma-atomic-emission spectrometry: A five element survey, Foren. Sci. Int. 17:253-263.

Hickman, D. A. (1984). Linking criminals to the scene of the crime with glass analysis, Anal. Chem. 56:844A-852A.

Horlick, G., Tan, S. H., Vaughan, M. A. and Shao, Y. (1987). Inductively coupled plasma-mass spectrometry, In: Inductively Coupled Plasmas in Analytical Atomic Spectrometry, (Montaser, A. and Golightly, D. W., eds.), VCH Publishers, NY, pp. 361-398.

Locke, J. (1980). The application of plasma source atomic emission spectrometry in forensic science, Analy. Chim. Acta 113:3-12.

Montaser, A. and Golightly, D. W., eds. (1987). Inductively Coupled Plasmas in Analytical Atomic Spectrometry, VCH Publishers, Inc., NY.

Swanson, R. C. (1986). Historical overview of product tamperings and highlights of current happenings, In: Response to Tampering of Food and Drug Consumer Products (Proceedings), Central States Association of Food and Drug Officials, Toledo, OH, pp. 5-13.

Wolnik, K. A., Fricke, F. L., Bonnin, E., Gaston, C. M. and Stazger, R. D. (1984). The Tylenol tampering incident - tracing the source, Anal. Chem. 56:466A-474A.

Wolnik, K. A., Gaston, C. M. and Fricke, F. L. (1989). Analysis of glass in product tampering investigations by inductively coupled plasma atomic emission spectrometry with a hydrofluoric acid resistant torch, J. Anal. At. Spectrom. 4:27-31.

APPENDIX I
FEDERAL ANTI-TAMPERING ACT

October 13, 1983

1365. Tampering with consumer products

(A) Whoever, with reckless disregard for the risk that another person will be placed in danger of death or bodily injury and under circumstances manifesting extreme indifference to such risk, tampers with any consumer product that affects interstate or foreign commerce, or the labeling of, or container for, any such product, or attempts to do so, shall -
  (1) in the case of an attempt, be fined not more than $25,000 or imprisoned not more than ten years, or both;
  (2) if death of an individual results, be fined not more than $100,000 or imprisoned for any term of years or for life, or both;
  (3) if serious bodily injury to any individual results, be fined not more than $100,000 or imprisoned not more than twenty years, or both; and
  (4) in any other case, be fined not more than $50,000 or imprisoned not more than ten years, or both.

(B) Whoever, with intent to cause serious injury to the business of any person, taints any consumer product or renders materially false or misleading the labeling of, or container for, a consumer product, if such consumer product affects interstate or foreign commerce, shall be fined not more than $10,000 or imprisoned not more than three years, or both.

(C) (1) Whoever knowingly communicated false information that a consumer product has been tainted, if such product or the results of such communication affect interstate or foreign commerce, and if such tainting, had it occurred, would create a risk of death or bodily injury to another person, shall be fined not more than $25,000 or imprisoned not more than five years, or both.
  (2) As used in paragraph (1) of this subsection, the term 'communicates false information' means communicated information that is false and that the communicator knows is false, under circumstances in which the information may reasonably be expected to be believed.

(D) Whoever knowingly threatens, under circumstances in which the threat may reasonably be expected to be believed, that conduct that, if it occurred, would violate subsection (a) of this section will occur, shall be fined not more than $25,000 or imprisoned not more than five years, or both.

Fine or imprisonment

(E) Whoever is a party to a conspiracy of two or more persons to commit an offense under subsection (a) of this section, if any of the parities intentionally engages in any conduct in furtherance of such offense, shall be fined not more than $25,000 or imprisoned not more than ten years, or both.

Investigation of violations

(F) In addition to any other agency which has authority to investigate violations of this section, the Food and Drug Administration and the Department of Agriculture, respectively, have authority to investigate violations of this section involving a consumer product that is regulated by a provision of law such Administration or Department, as the case may be, administers.

Definitions

(G) As used in this section -
  (1) the term "consumer product" means -
    (A) any "food", "device", or "cosmetic", as those terms are respectively defined in section 201 of the Federal Food, Drug, and Cosmetic Act (21 U.S.C. 321); or
    (B) any article, product, or commodity which is customarily produced or distributed for consumption by individuals, or used by individuals for purposes of personal care or in the performance of services ordinarily rendered within the household, and which is designed to be consumed or expended in the course of such consumption or use;
  (2) the term "labeling" has the meaning given such term in section 201(m) of the Federal Food, Drug, and Cosmetic Act (21 U.S.C. 321(m));
  (3) the term "serious bodily injury" means bodily injury which involves -
    (A a substantial risk of death;
    (B) extreme physical pain;
    (C) protracted and obvious disfigurement; or
    (D) protracted loss or impairment of the function of a bodily member, organ, or mental faculty; and
  (4) the term "bodily injury" means -
    (A) a cut, abrasion, bruise, burn, or disfigurement;
    (B) physical pain;
    (C) illness
    (D) impairment of the function of a bodily member, organ, or mental faculty; or
    (E) any other injury to the body, no matter how temporary

NOTE: The maximum fines listed above have been increased dramatically by the passage of the Criminal Fines Enforcement Act, October 30, 1984

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ANALYSIS OF EXPLOSIVES

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Analysis of explosives is one of the most challenging examinations undertaken by forensic scientists. Questions from investigators are wide ranging: for example, "is this substance an explosive?"; "what was used to blow up the car?"; "did an explosion cause the aircraft to crash?". Exhibits range from unreacted particles of propellant powder through explosion-shredded clothing to garbage cans full of miscellaneous debris.

To best answer such questions and to obtain maximum information from the examinations, the scientist will have spent considerable time observing test explosions, collecting explosion-damaged material and chemical residues, and conducting systematic analyses of explosives of known composition and their residues (Beveridge 1986). He or she also must have current knowledge of chemical compositions of commercial, military and improvised explosives; of recovery and clean-up methods for residues of explosives; and of application of appropriate and sensitive analytical methods.

Methods currently used in major forensic laboratories conducting analyses of explosives have advanced dramatically in the past decade and permit recovery and identification of smaller and smaller amounts of explosives. The development and application of these analytical methods are surveyed and their place in systematic analyses of post-explosion debris is discussed and illustrated.

CLASSIFICATION OF EXPLOSIVES

The forensic scientist normally deals with explosives which can be classified as deflagrating or detonating.

Deflagrating explosives or low explosives are substances or mixtures which burn rapidly when ignited by flame while unconfined and which, if confined, can explode to rupture and fragment the container. Commercial examples are propellants like smokeless powders, black powder, and pyrotechnic compositions. These and improvised chemical mixtures frequently are encountered in casework as fillers for pipe bombs. Black powder is a typical low explosive with a detonation velocity of approximately 400 ms^{-1}.

Detonating explosives or high explosives are designed to shatter and are initiated by shock (blasting cap). They do not have to be confined and typically explode at detonation velocities in the range of 2000 to 9000 ms^{-1}. Examples include commercial dynamites, slurries, emulsions, and detonating cords, and military demolition and plastic explosives.

Detailed information on explosive compositions, chemistry, structural formulae, etc., may be found in the four-volume series "Chemistry and Technology of Explosives" by Urbanski (1964, 1965, 1967, 1984) and the ten-volume "Encyclopedia of Explosives and Related Items" (1960-1983) produced in the U. S. by Picatinny Arsenal (vols. 1 - 8) and the U. S. Army Armament Research and Development Command (vols. 9 and 10). A useful discussion of the fundamental aspects of explosives may be found in a paper by Urbanski and Vasudeva (1981).

DEVELOPMENTS IN ANALYTICAL METHODOLOGY

Advances in methodology are published both in scientific journals and in monographs. The latter provide four useful compendia of methods. "The Analysis of Explosives" by Yinon and Zitrin (1981) describes methodology published up to 1980 and although many advances have been made since then, it still provides a wealth of useful, well organized information. Triennial international symposia on the analysis and detection of explosives have been held since 1983. The Proceedings (1983, 1989) of the first and third meetings in the U. S. and Germany respectively were published as monographs. The Proceedings (1986) of the second meeting in Israel were published as a special edition of the Journal of Energetic Materials which included a review of the literature from 1980 to 1986 by Beveridge (1986). Another literature review for the same period was published by Washington and Midkiff (1986).

Many of the developments cited in the literature have been incorporated into schemes for the systematic analysis of explosives and their residues. The additions have primarily reflected advances in the sensitivity and selectivity of instrumental analysis. For example, the systematic analysis scheme of Amas and Yallop (1966, 1969) consisted solely of spot tests but when combined with the TLC systems of Jenkins and Yallop (1970), it provided a general scheme for identification of many commonly-encountered explosives and their residues. Beveridge *et al.* (1975) amplified the scheme by addition of infrared spectroscopy (IR), for organic and inorganic components and X-ray powder diffraction (XRPD), emission spectrography and polarizing microscopy for inorganic components.

The next stage of development was analysis of organic components of explosives by gas chromatography (GC) and high performance liquid chromatography (HPLC), and analysis of inorganic components by ion chromatography (IC), HPLC and SEM/EDX.

The three GC detectors most often used for explosive analysis are the electron capture detector (ECD), the chemiluminescence thermal energy analyzer detector (TEA) and the mass spectrometer (GC/MS). Prior to the application GC/TEA analysis the most popular GC method for explosive analysis was GC/ECD using fused silica capillary columns (Douse 1982) preferably with a cold on-column injector (Penton 1983). Douse (1983) then reported that GC/TEA had sensitivity similar to GC/ECD but greater selectivity and was much less prone to fouling by contaminants. Further, being a more selective detector than ECD, less sample cleanup was required. The original claims of Fine *et al.* (1984) that clean-up was not required for TEA analysis did not take into account the effect on fused silica capillary columns of repeated injections of dirty samples. At least a guard column is required for protection of the analytical column and clean-up should be undertaken. Modifications to improve GC/TEA chromatographic performance have been described by Douse (1987) and Collins (1989). The application of GC/MS to explosives has been reviewed by Yinon and Zitrin (1981) and Yinon (1982, 1987) and discussed in detail by Zitrin (1986).

The use of HPLC in explosive analysis has been reviewed by Krull (1983). Three HPLC detectors are currently in routine use - electrochemical, TEA, and ultraviolet (UV). Lloyd (1983c) introduced the application of a pendant mercury drop electrode (HPLC/PMDE) electrochemical detector which had similar sensitivity to GC/ECD but was much less susceptible to fouling by contaminants. The TEA detector (Fine *et al.* 1984) is a selective nitro-nitroso detector which is used much more widely than electrochemical detectors (Selavka *et al.* 1988). HPLC/TEA is not without its limitations; for example, it cannot be used with a reverse phase system, or, without modification, for sensitive analysis of nitroaromatics. Neither is a major drawback, however, as demonstrated by the wide range of commercial and military explosives analyzed by HPLC/TEA (Fine *et al.* 1984) and by a modification introduced by Selavka *et al.* (1988) to improve sensitivity for nitroaromatics. UV detectors have given way to the more selective and sensitive TEA detectors for screening and for confirmation, but still have several specific applications which will be noted below. Rudolph and Bender (1983) used a UV detector in series with a TEA detector.

Analysis for inorganic ions by IC (Ruetter *et al.* 1983a) permitted improved sensitivity and identification of ionic species which were decomposed by evaporation of aqueous extracts. HPLC/UV was applied to identification of ions like nitrate and nitrite (Skelly 1982). SEM/EDX permitted non-destructive elemental analysis with a degree of sensitivity which made many spot tests redundant.

Several of these techniques were incorporated into general schemes for analysis of explosives and residues by Rudolph and Bender (1983) (HPLC/TEA, GC/MS, IC) and Garner *et al.* (1986) (GC/TEA, HPLC/TEA, IC, SEM/EDX).

Other methods such as HPLC/MS (Yinon and Hwang 1983), thermospray HPLC/MS (Voyksner and Yinon 1986; Berberich *et al.* 1988), MS/MS (McLuckey *et al.* 1985; Yinon 1988) and SFC/TEA (Douse 1988) may become more routinely used as their application is extended from pure explosives to a comprehensive range of residues from test explosions and as they offer affordable improvements in selectivity, sensitivity and ease-of-use over present methods.

SYSTEMATIC ANALYSIS OF EXPLOSIVES AND EXPLOSIVE RESIDUES

The key steps to systematic analysis of explosives and residues from explosives are as follows.

1 — Recover the unreacted explosive and/or its chemical residue from the material in or on which it has been deposited.

2 — Clean-up the recovered explosive to remove co-extractives. This step is not required when dealing with samples of uncontaminated, unreacted explosive or explosive vapors but is often essential with solvent extracts not only to facilitate identification but also to protect chromatographic columns and detectors.

3 — Analyze and identify the components of the explosive. The more common options for these steps are considered next.

I - Recovery

Vapor recovery: The normal first step in systematic analysis of post-explosion debris is to recover any residual explosive vapors. This procedure is particularly effective with respect to recovery of ethyleneglycol dinitrate and nitroglycerine (glycerol trinitrate) from dynamite. The debris is sealed in a suitable container, for example a can, and the headspace vapor is pumped through a tube packed with an adsorbent chemical. Charcoal or Tenax (a proprietary polymeric adsorbent) are most commonly used. Prime and Krebs (1980), Rudolph and Bender (1983) and Garner *et al.* (1986) have described similar procedures for drawing vapor through a charcoal tube from which adsorbed explosives were eluted for subsequent analysis. In a different approach, Wardleworth and Ancient (1983) used a portable, heated metal disc to thermally desorb explosive vapors from surfaces such as car seats. Explosive vapors were drawn through a tube containing Tenax from which residues were recovered by elution with ethyl acetate. Lloyd (1985a) has reviewed the adsorption characteristics of several adsorbents and notes that charcoal is particularly useful for recovery of EGDN and NG since it has a negative selectivity for these explosives.

Our own studies of adsorbents for explosive vapors in air at explosive scenes have led us to use tubes containing Tenax combined with a portable pump both at a scene and for recovery of vapors from debris examined in the laboratory (Deak *et al.* 1989).

Microscopic examination: Once headspace vapors have been recovered, the next step is to examine the debris using a stereobinocular microscope. In conducting microscopic examinations, there is no substitute for the experience gained by prior examination of debris from test explosions of known explosives and IEDs. For example, smokeless powders may often be recognized and recovered unreacted or only partially burned. Sometimes traces of unreacted detonating (high) explosives and their wrappers may be recovered. Even if unreacted explosive or products from explosives are not observed, the explosive damage may suggest the most effective way of conducting the next step - isolation of explosive residues. For example, deflagrating (low) explosives have to be confined to be effective, so fragments which appear to have originated from a container probably are good sources of residue. Likewise, any physical evidence of an IED such as wrappers, tape, batteries, timers, electronic parts, etc., must be recognized and recovered and examined for residue. If the question is "did an explosion occur?", the presence of microcraters in metal can provide the answer, as can metallurgical examination of metal fragments (Tardif and Sterling 1967).

When unreacted explosives or crystals, etc., are observed, every effort should be made to isolate them without altering their physical state. Scalpels and dissecting needles are well suited for this. If this is not possible, then material which is explosion-damaged or appears to bear residue is subjected to the next stage of the procedure - recovery of traces of explosives usually by solvent extraction.

Debris extraction: Extraction of debris usually is undertaken by successive organic and aqueous solvent washes or by swabbing, with the procedure followed being dictated by what is necessary to extract the maximum quantity of explosive residue and the minimum quantity of contaminants. The end result usually is usually an extract of organic compounds, an aqueous extract of inorganic compounds, and an insoluble residue. The general guideline is to use as little solvent as possible, and to use solvents which will maximize explosive recovery while minimizing recovery of co-extractives.

In general approaches to debris extraction, Beveridge *et al.* (1975) used ether, acetone and water, Rudolph and Bender (1983) used acetone and water, and Garner *et al.* (1986) used acetone and/or dichloromethane and water. Douse (personal communication) used methyl t-butyl ether (MTBE) to extract debris for organic explosives and has described the procedure as applied to hand swabs (Douse 1985; Douse and Smith 1986). Lloyd (1985b) used methanol to extract organic explosives and described the procedure as applied to hand swabs and post-explosion debris.

II - Clean-up

Regardless of the solvent used, other material is likely to be co-extracted along with any explosives. Twibell *et al.* (1982) used preparative TLC to clean-up ethanol extracts of NG from hand swabs. Douse (1985) cleaned-up MTBE hand swab extracts by retaining them on a short column of Amberlite XAD-7 resin while eluting the co-extractives with pentane. The explosives were recovered with ethyl acetate. Douse and Smith (1986) improved the method by varying the composition of the column eluent (pentane/MTBE) depending on how dirty the MTBE hand swabs were. Lloyd (1985b) described a clean-up procedure for hand swabs which used a centrifugal microfilter containing Porapak T resin - a more robust form of Amberlite XAD-7. Lloyd and King (1990) have described solid phase extraction and clean-up of swabs of explosives and gunshot residue which minimizes handling by conducting the procedure entirely within the container in which the sample was received. Chromosorb 104 and Amberlite XAD-4 resin were used.

Water extracts are normally cleaned by passing them through a membrane filter to remove any solid material. Ordinary filter paper is not recommended since traces of nitrate ion can be extracted from filter paper in sufficient concentration to be recorded by ion chromatography (Gallicano and Beveridge, unpublished results).

III - Analysis

Analysis of particles: Samples of uncontaminated explosives, for example, powders, plastics, gels, emulsions - and uncontaminated, physically recovered residues are analyzed firstly by IR and SEM/EDX. This identifies the class of explosive and the elemental composition. If necessary, the explosive or residue will then be subjected to solvent extraction to divide its components into organic, inorganic and insoluble fractions.

Analysis of organic extracts: The organic extract can contain nitrate esters like nitroglycerine (NG) and pentaerythritol tetranitrate (PETN) characterized by the C-O-NO_2 group, nitramines like cyclotrimethylenetrinitramine (RDX) characterized by the N-NO_2 group and organic nitrates like trinitrotoluene (TNT) characterized by the C-NO_2 group.

General schemes for systematic analysis of organic extracts began with spot tests and TLC and evolved first to IR and TLC (Beveridge *et al.* 1975) and then to HPLC and GC/MS (Rudolph and Bender 1983) and TLC, HPLC-TEA and GC-TEA (Garner *et al.* 1986).

There are different views as to which combination of instrumental methods is optimum for positive identification of an organic explosive. With clean extracts, for example, from particles of unreacted explosive or from metal fragments, no more than TLC and IR may be required. However, the greater the contamination, the greater the potential interference with IR spectra, and the greater the need to use more selective and sensitive procedures

Fine *et al.* (1984) expressed the view that combined GC/TEA and LC/TEA analysis of organic explosives is definitive if three criteria are met:

1 — the peak elutes at the proper retention time on both GC/TEA and HPLC/TEA,
2 — both chromatograms are relatively clean, and
3 — identical quantitation is achieved on both systems.

In support they noted that the TEA detector is selective for nitrated organic compounds (Goff *et al.* 1983), and that GC and HPLC separations are achieved by different mechanisms - GC separation is based on differences in vapor pressure and solubility whereas HPLC separations are based on differences in polarity, size and shape. This approach was used by Garner *et al.* (1986) in their systematic analysis scheme which used combined GC/TEA and HPLC/TEA for confirmation of explosives tentatively identified by TLC.

Lloyd (1986b) took the view that use of entirely different detectors was preferable to using the same TEA detector for two different separation techniques and has used GC/TEA to confirm HPLC/PMDE analysis of traces of propellants from firearms. He also expressed the view that use of one technique with columns of different selectivity would provide mutual confirmation. Such different columns have, indeed, been used for identification of explosives by GC/TEA (Douse and Barnes, personal communication).

Zitrin (1986) has compared explosive analysis to drug analysis and argued that identification criteria for explosives must match those for drugs, that is, identification must be based on spectroscopic analysis rather than on chromatography (or spot tests). He described the criterion of the Israel Police Laboratory to be that identification of an organic compound should not rely only on chromatographic methods even when several combinations of these are applied. He pointed out that one reason why many labs rely on chromatographic methods for explosive analysis is that spectroscopic methods (IR, MS, NMR) are rendered ineffective for identification of explosive residues due to contamination by coextractives even in extracts subject to clean-up procedures. He argued that these problems are overcome by using TLC as a screening method followed by positive identification by GC/MS . Casework examples were cited (Zitrin 1986; Tamiri and Zitrin 1986). In a similar approach, Rudolph and Bender (1983) used HPLC/TEA as a primary analytical method for organic explosives and used GC/MS for confirmation.

In the RCMP laboratories our approach is to use whatever combination of GC/TEA, HPLC/TEA, GC/ECD, TLC, IR and GC/MS is required to reach a forensic conclusion under the circumstances of the case - and which will withstand any challenges in court.

Analysis of aqueous extracts: Our usual approach is to analyze a small portion of the aqueous extracts by IC (Ruetter *et al.* 1983a), evaporate the remainder to dryness and then analyze the residue by SEM/EDX and by IR using a diamond cell and a fourier transform infrared spectrometer (FTIR). Spot tests may be used for screening large quantities of residue but they and the polarizing microscope have largely been replaced by sensitive and definitive instrumental analyses. In the case of trace quantities of residues, much more information can be gleaned by non-destructive IR and SEM/EDX than by destructive and non-definitive spot tests. XRPD is still used if necessary.

Analysis of insoluble residues: Insoluble residues are often neglected but can yield useful information - especially those residues which are retained on explosive damaged material after all solvent extractions. The primary analytical methods are IR and SEM/EDX, plus XRPD if required. Typical insoluble residues are manganese dioxide from batteries, aluminum and carbonaceous fuel, barium sulphate, calcium salts, gums, etc.

Analysis of five-year-old debris: The previous discussion of schemes for systematic analysis has highlighted approaches for analyzing debris for unknown explosive residues. These schemes, old and new, offer guidelines and alternatives which are subject to testing and to change as the efficacy of new methods is proven. The following case-note describes the procedures used to resolve one aspect of a major international bombing incident in which a bomb manufactured in Canada exploded in the baggage handling area of a Japanese airport causing the death of two baggage handlers.

In 1989 we studied procedures to clean-up very contaminated solvent extracts of shredded clothing from test explosions (Gilmour and Beveridge, unpublished). Microcolumns of Amberlite XAD-7 resin (Douse 1985) and Poropak T resin (Lloyd 1985b) designed to retain explosives on the column, while eluting the contaminants, were ineffective because of the high concentration of the coextractives. We then used a macrocolumn of 2 cm of activated charcoal over 10 cm of activated silica gel which effectively retained much of the coextracted plastic and dyes on the column. The explosive was eluted with approximately a 3:2 mixture of hexanes (petroleum ether) and acetone and was identified in several successive 1 ml aliquots of eluate by GC/TEA analysis. The ultimate test of the system was acetone extraction of casually-bagged clothing debris from a dynamite test explosion conducted five years earlier. Ethyleneglycol dinitrate (EGDN) and NG were recovered and shown to be present by GC/TEA.

This unexpected finding led us to obtain and examine five-year old exhibits in the previously-noted fatal bombing incident in which dynamite was suspected but not proven. The silica gel clean-up procedure was applied to acetone extracts of explosion-shredded clothing which had been contaminated by such substances as water, dry chemical fire extinguisher powders, building products and blood. EGDN and NG in very low concentration were indicated by GC/TEA in some eluate fractions and an HPLC/TEA screen with some very small aliquots supported the GC/TEA results. For confirmation, the extracts were analyzed using GC/MS with chemical ionization (GC/CIMS) using methane gas and selective monitoring of three ions for EGDN and for NG. The remaining samples were then subjected to HPLC/TEA analysis which required 10x more eluate than GC/TEA or GC/CIMS. These combined analyses confirmed the presence of dynamite and tied in with earlier identification of nitrate ion (IC, IR) and insoluble barium sulphate (SEM/EDX, IR). The identification of dynamite, combined with much other circumstantial evidence presented to the court by police and forensic scientists from two continents, led the judge to convict the suspected bombmaker of manslaughter.

A successful analytical outcome notwithstanding, some eluates of the clean-up procedure did still contain sufficient co-extractives to foul and block first the GC capillary guard column and then the analytical column. Only one injection was made using GC/ECD analysis; it resulted in no useful data and totally incapacitated the detector - yet the same sample was successfully analyzed by GC/TEA, HPLC/TEA and GC/MS. In this case - and in many others - the sample size and contamination problems would have prevented detection not only by GC/ECD but also by the much less sensitive TLC and IR. This underlines the value of the selective and sensitive TEA and MS procedures used.

ANALYSIS OF SPECIFIC EXPLOSIVES

The methods used in general schemes for systematic analysis of explosive residues are derived from instrumental methods and techniques which have been successfully applied to analysis of specific types of explosives. The following discussion is of techniques and methods currently applied to some of the more commonly encountered classes of explosives - commercial propellants, chemical mixtures based on nitrates, chlorates and perchlorates, military explosives, commercial high explosives and some less common explosives.

I - Commercial Propellants

Black powder and pyrodex: Classical black powder is a mixture of potassium nitrate, sulphur and charcoal in a typical ratio of 75/10/15. Some black powders contain cheaper sodium nitrate. In the mid-1970s an explosive named Pyrodex was developed in the USA as a safer alternative to black powder. Its formulation contained potassium perchlorate, sodium benzoate and dicyandiamide as well as the traditional black powder ingredients.

In black powder, IR spectroscopy or x-ray powder diffraction (XRPD) identify nitrate, and spot tests or SEM/EDX identify sulphur and the alkali metal. Carbon is usually identified by elimination. In pyrodex, IR and XRPD also identify perchlorate.

Beveridge *et al.* (1975) used IR to identify potassium sulphate, carbonate, nitrate and thiocyanate in residues from various test explosions of black powder. The composition varied from test to test except for the presence of potassium sulphate. Rudolph and Bender (1983) used IC to identify potassium, sodium, sulphate, nitrate and nitrite ions in the aqueous extract of black powder residue and chlorate, chloride, nitrate, nitrite and sulphate in the residue of burned pyrodex. Bender (1986a) used HPLC with indirect photometric detection to analyze residue from the burning of black powder and pyrodex. He detected nitrate ion in unreacted black powder and nitrate and perchlorate in unburned pyrodex. In the residue from burned black powder he detected nitrite, sulphate, sulphide, thiocyanate and carbonate; in the residue of burned pyrodex he detected perchlorate, chlorate, chloride, nitrate, nitrite, sulphate, sulphide and thiocyanate. Bender (1986b) described the primary residue from burning of pyrodex to be potassium carbonate, sulphate and chloride but expressed reservations about the forensic significance of potassium chloride in a real world situation since it is a possible environmental contaminant and can be formed by reaction in a polyvinylchloride pipe. His approach to positive identification of pyrodex residue was to identify the components sodium benzoate and dicyanamide by HPLC using a variable wavelength UV detector.

As noted earlier, our normal procedure is to analyze an aliquot of aqueous extract by IC, evaporate the rest and analyze the resultant solid by IR and SEM/EDX.

Smokeless powder: There are three categories of smokeless powder - single base (nitrocellulose; NC), double base (nitrocellulose plus nitroglycerine; NG) and triple base (nitrocellulose, nitroglycerine and nitroguanidine). Single base powder is used primarily in rifle ammunition, double base in pistol and shotgun ammunition and triple base in military ordnance. Smokeless powders are manufactured in several different shapes which influence the burning rate and with additives to enhance stability (for example, diphenylamine, centralites), to modify burning (for example, dinitrotoluene, potassium sulphate) and to act as plasticizers (for example, dibutyl phthalate, ethyl centralite - 1,3 diethyl 1,3 diphenyl urea).

Single and double base powders are commercially available for handloading and frequently are used as pipe bomb fillers. There have been no reports in the literature of such use for the larger-grained triple base powder. The monograph "Propellant Profiles" (1988) lists forensically useful properties such as particle size, shape and velocity of detonation for many common smokeless powders; the description of powders as single and double base is a useful but not infallible guide.

When smokeless powder is used in an IED it frequently is recovered as unburned or partially burned particles. This permits morphological measurements and comparison with data bases. The combination of TLC and IR permits unambiguous discrimination of single and double base powder. Organic additives may be analyzed by TLC and/or by instrumental methods like HPLC/UV, GC/FID or GC/MS. Inorganic additives like potassium sulphate can be identified by IC or a combination of SEM/EDX and IR. When individual particles are not apparent as in hand swabs or with miscellaneous debris, then more sensitive methods such as GC/TEA and HPLC/PMDE may be required and the results interpreted with caution if only nitrocellulose or diphenylamine are identified since they have non-explosive applications in the environment.

We prefer to use TLC plus IR for smokeless powder identification. Inorganic components like potassium sulphate are readily identified by aqueous extraction of particles followed by analysis by IR and SEM/EDX.

Jenkins and Yallop (1970) described several TLC systems which separate NC (Rf 0) from NG (Rf about 0.2 to 0.6). Archer (1975) took TLC of smokeless powders a step further by describing six solvent elution systems and six developing reagents for separation and visualization of minor components (additives and byproducts) such as diphenylamine, nitro- and nitrosodiphenylamines, nitrotoluenes, phenyl- and ethyl-substituted ureas (centralites) and nitroguanidine. The combination of Archer's elution systems and reagents allowed at least two systems to be applied to each additive.

Several instrumental methods of analysis have been applied to smokeless powder additive identification. Bender (1983) used HPLC with sequential UV and TEA detectors to identify nanogram quantities of diphenylamine and its N-nitroso and 2-nitro- derivatives, 2,4 and 2,6 dinitrotoluene, nitroglycerine, and n-butyl phthalate. DeBruyne *et al.* (1989) used HPLC with a diode array UV detector to identify substituted urea additives (centralites); the diode array permits the UV spectrum to be recorded. Mach *et al.* (1978) analyzed unreacted smokeless powders by GC/MS with methane chemical ionization (CIMS) and identified nitroglycerine, 2,4 dinitrotoluene, diphenylamine, dibutyl phthalate and ethyl centralite but were unsuccessful in applying the technique to positive identification of unreacted powder in residues. Selavka *et al.* (1989) found that IC was useful in discriminating morphologically similar ball powders and used gas chromatography GC/FID to determine the plasticizers dibutyl phthalate and ethyl centralite. TLC was used to distinguish single and double base powders. They described a computer program which used size, shape and chemical composition of smokeless powders to determine the manufacturer. Keto (1989a) noted that pyrolysis gas chromatography had only limited value for source identification of smokeless powders.

Smokeless powder may be encountered as organic gunshot residue on the skin (primarily as hand swabs) and on clothing. The small quantities recovered from these swabs coupled with contamination problems have required development of methodology for NG and NC which is more sensitive and selective than required for relatively large IED residues. Jane *et al.* (1983) based their methodology on TLC and GC/ECD. Lloyd (1983a) used microcolumn cleanup procedures followed by analysis by HPLC/PMDE to recover and identify NG gunshot residue from clothing. Lloyd (1984, 1986a) identified nitrocellulose in gunshot residue by microcolumn cleanup followed by size exclusion chromatography using a PMDE. Lloyd (1986b, 1987) detailed his methodology and its application to smokeless powder both unreacted and as gunshot residue and critically assessed the significance of finding diphenylamine or nitrocellulose in extracts of debris or swabs as opposed to components of recognizable smokeless powder particles; he also noted that GC/TEA had become a complementary technique to his HPLC/PMDE method. In a further refinement of cleanup procedures, Lloyd and King (1990) described the recovery of explosive traces including gunshot residue from swabs without removing the swab from the container in which it was received. Douse (1985) determined that a cleanup procedure using an XAD-7 Amberlite resin followed by capillary GC/TEA analysis enabled low nanogram levels of explosives including NG to be identified in handswabs.

Kee *et al.* (1990) took a different approach to smokeless powder gunshot residue analysis. It was based on infrared analysis of the methanol extract of a suspected propellant particle to identify nitrocellulose followed by GC/MS analysis using electron impact excitation to identify nitroglycerine, diphenylamine, ethyl centralite and dinitrotoluene.

II - Chlorates and Perchlorates

Perchlorate compounds are used in the formulation of commercial explosives such as flashpowders, pyrodex (potassium salt) and emulsions (sodium and ammonium salts). Chlorates and perchlorates are frequently used in IEDs. Both are strong oxidizing agents and typically are combined with such fuels as aluminum, sugars or alkali metal benzoates and salicylates.

Commercial mixtures of such chemicals are referred to as flash powders.

Perchlorate mixtures in IEDs usually leave sufficient unreacted perchlorate in solid residues or in evaporated aqueous extracts to permit identification by IR or XRPD. IC can also be used. The major products are chlorate and chloride. The chlorate can be identified by IR or XRPD if present in sufficient quantity, or by IC. Chloride is not detected by IR but is readily identified by XRPD and IC.

Chlorate mixtures yield chloride as the major product and there is usually sufficient unreacted chlorate to identify by IR.

Meyers (1978) published a systematic approach to flash powder analysis based on aqueous extraction followed by spot tests and IR. This was updated by Midkiff (1989) through addition of further spot tests, XRPD and ion chromatography. Beveridge *et al.* (1983) used XRPD and IR to identify unreacted potassium perchlorate and also chloride- and chlorate- condensed reaction products in residues of mixtures of perchlorates with aluminum and with sugar. Fung (1986) used the same techniques to identify perchlorate/benzoate and perchlorate/salicylate mixtures (from whistling fireworks (Conklin 1981) in pipe bomb residues. Reutter and Buechele (1983) noted that suppressed IC for perchlorate required a specific column and eluent. Green (1986) used unsuppressed IC to identify chloride, chlorate and perchlorate in the residue from perchlorate/sugar pipe bombs. Identification of pyrodex residue has been dealt with above.

Rudolph and Bender (1983) identified chloride and chlorate in chlorate/sugar residue by IC, and Beveridge *et al.* (1983) obtained the same results using IR and XRPD. Ruetter *et al.* (1983a) analyzed chlorate residue both by IC and by XRPD and showed by that some 50% of the chlorate was reduced to chloride during evaporation. The IC system originally used by Rudolph and Bender (1983) did not permit separation of nitrate and chlorate ions but the system manufacturer subsequently introduced new analytical columns which have resolved this problem (for example, AS9 analytical column and AG9 guard column; Dionex, Sunnyvale, CA). Beveridge et al (1983) identified sugar residues using IR and XRPD for unreacted material and GC/MS of trimethyl silylated derivatives for the syrups resulting on evaporation. Nowicki and Pauling (1988) used the same GC/MS protocol and expanded it to sugars other than sucrose, glucose and fructose.

III - Nitrates

Nitrates are widely used in the commercial explosives industry. They are an integral part of the formulation of dynamites, slurries and emulsions, and are also used in improvised explosive devices.

Methods typically used for analysis of nitrates are IR, IC XRPD and HPLC. Some of these have already been discussed.

Beveridge *et al.* (1983) used IR and XRPD to identify nitrate, nitrite, carbonate and bicarbonate in residues of nitrate/sugar pipe bombs. We now routinely analyze for nitrate by IC and IR. When the IC results cannot be confirmed by IR (or XRPD), that is, due to interference by other species, we seek confirmation of IC results by adapting a reversed-phase HPLC method which was used by Skelly (1982) with a UV detector to identify nitrate and nitrite in acid, water and silage. By employing a diode array UV detector, traces of nitrate and nitrite were readily detected by their UV spectra as well as retention time even in the presence of excess phosphate, bicarbonate and sulphate from fire extinguisher powders (Gallicano and Beveridge, unpublished results).

Two papers from Israel offered a different approach to nitrate recovery and identification. Glattstein and Kraus (1986) used the oxidizing properties of ions such as nitrate and chlorate to selectively transfer the ions to an organic phase by use of lipophilic quaternary ammonium cations thus separating them from other ions like sulphate, carbonate and nitrite. The extracted ions were identified by IR and spot tests. Woolfson-Bartfeld *et al.*

(1989) used reversed-phase ion-pair liquid chromatography with indirect UV detection to detect ions typically found in low explosive IED residues including nitrate.

IV - Military Explosives

The most commonly encountered military explosives are trinitrotoluene (TNT), pentaerythritol tetranitrate (PETN), and the nitramines RDX and HMX. RDX and HMX are British acronyms for Research Department Explosive and High Melting Explosive respectively. They are otherwise known as cyclotrimethylene trinitramine and cyclotetramethylene tetranitramine. TNT is a demolition explosive and is a component, with HMX, of the explosive octol. PETN is a demolition explosive which may be encountered in several different forms, for example, blocks, cords or sheets, and is a component, with RDX, of the plastic explosive Semtex-H. RDX is the primary component of the plastic explosive C4.

Military explosives have been analyzed by IR, XRPD, TLC, capillary GC/MS, GC/TEA, GC/ECD, HPLC/TEA, HPLC/PMDE, SFC/TEA, and gel permeation chromatography. Our normal procedure involves GC/TEA, HPLC/TEA, IR and GC/MS.

Douse (1982) has described TLC systems for TNT, PETN, RDX and HMX. Since each of these four explosives is a crystalline solid, IR and XRPD are also appropriate methods of analysis. Where greater sensitivity is required, GC methods may be applied. Douse (1983) and Fine *et al.* (1984) analyzed TNT, PETN and RDX by GC/TEA. Fine *et al.* (1984) analyzed TNT, PETN RDX and HMX by HPLC-TEA. Selavka *et al.* (1988) used photolytically assisted HPLC-TEA analysis to improve the detection of TNT. Douse (1988) successfully analyzed TNT, PETN and RDX by supercritical fluid chromatography/TEA (SFC/TEA) but noted that HMX had a poor peak shape.

Twibell *et al.* (1984) studied the persistence of traces of TNT, PETN and RDX, on the hands, using GC/ECD for analysis. Douse (1985) used GC/TEA to identify TNT and RDX in handswab extracts which had been cleaned-up using a column of Amberlite XAD-7 resin. Lloyd and King (1989) used complementary analysis by GC/TEA and HPLC-PMDE to identify Semtex (PETN/RDX) recovered from handswabs cleaned-up by centrifuging and passing through a microcolumn packed with Amberlite XAD-4 resin.

Keto (1986) has published a procedure for the extraction, separation and identification of the main components of C4 - RDX, the plasticizer and the rubber binder. Keto (1989b) has also conducted detailed analysis of Semtex-H using HPLC/UV to ratio RDX and PETN, and gel permeation chromatography (size exclusion chromatography) to separate RDX, PETN, a styrene-butadiene copolymer binder and an antioxidant. He used TLC to identify the dye in the explosive. Hexane was used to extract hydrocarbon oil. HPLC/TEA identified HMX impurities in USA-made C4 but not in Semtex (Czech).

Tamiri and Zitrin (1986) have given several examples of the application of TLC and capillary GC/MS to the analysis of post-explosion debris including identification of TNT, PETN and RDX. Yinon (1982, 1987) has published reviews on mass spectrometry of explosives which included electron impact, positive ion and negative ion chemical ionization spectra of TNT, PETN, RDX and HMX. Basch *et al.* (1986) have used GC/MS and nuclear magnetic resonance (NMR) to identify lower nitrate esters of PETN in post-explosion debris.

V - Commercial High Explosives

Dynamites: Dynamites were named by Nobel after the Greek word "dynamis" meaning power. They are mixtures of five basic components - ethylene glycol dinitrate (EGDN), glycerol trinitrate (nitroglycerine; NG), nitrocellulose (NC), inorganic nitrates and fuels. EGDN and NG are the ingredients which define an explosive as dynamite and serve both as sensitizers and fuels. Dynamites which contain NC are called gelatines. The inorganic nitrates are oxidizing salts. Most dynamites contain sodium nitrate (SN) to enhance the oxygen balance (Urbanski and Vasuveda 1981) and many contain ammonium nitrate (AN) which replaces some of the nitroglycerine in the formulation and makes the dynamite an ammonia dynamite. Other fuels consist of such materials as starch, wood pulp, coconut husks and gums. Other additives are sometimes included such as barium sulphate in seismic dynamite to enhance propagation under a high hydrostatic head.

Dynamite is primarily analyzed by instrumental methods, especially GC/TEA, HPLC/TEA, GC/ECD, GC/MS, and HPLC/PMDE (Lloyd 1093c) for EGDN and NG, and IC, IR and XRPD for soluble inorganic components and products. Insoluble residues are analyzed by such methods as SEM/EDX, IR and XRPD. TLC and selected spot tests also remain viable for particle analysis.

We typically use GC/TEA, complemented by HPLC/TEA and/or by GC/MS for NG and EGDN, if required, IC and IR for AN, and IR and SEM/EDX and sometimes XRPD for aqueous extracts and insoluble components.

Beveridge *et al.* (1975) analyzed dynamite and its residues by successive solvent extraction by ether, acetone and water. Ether extracted EGDN and NG which were analyzed by IR and TLC. Acetone extracted NC and some AN which also were analyzed by IR and TLC, and water extracted SN, AN, and in the case of residues, products which were sodium sulphates and carbonates. The inorganic salts were analyzed by IR and XRPD. Insoluble material consisted of unreacted carbonaceous fuel which was analyzed by spot tests, and of chemicals such as barium sulphate which were analyzed by IR and XRPD. Similar techniques for dynamite analysis were described in the same era by Midkiff and Washington (1974).

GC analysis of EGDN and NG was made routine by use of fused silica capillary columns (Douse 1981) and cold on-column injectors (Penton 1983). EGDN and NG were detected at low picogram levels by GC/ECD (Douse 1981) and by GC/TEA (Douse 1983; Fine *et al.* 1984). Douse (1985) compared GC/TEA and GC/ECD for detection of EGDN and NG in handswab extracts and concluded that TEA detection approached the sensitivity of ECD but was more selective. Casework examples of detection of EGDN and NG in post-explosion debris using GC and GC/MS have been given by Zitrin (1986) and Tamiri and Zitrin (1986). Zitrin (1986) made the very important point that electron impact conditions led to production of only uncharacteristic, low molecular weight fragments whereas methane chemical ionization (CIMS), provided a characteristic fragmentation pattern (Yinon 1982, 1987).

EGDN and NG have been successfully analyzed by HPLC/TEA Fine *et al.* (1984), HPLC/PMDE (Lloyd 1983a) and HPLC/UV (Prime and Krebs 1980).

Twibell *et al.* (1982) compared TLC, GC/ECD and GC/MS for detection of nitroglycerine in handswabs from persons who had handled dynamite and selected GC/ECD as the most suitable method. Lloyd (1983b) used HPLC/PMDE to identify nitroglycerine on handswabs from the hands of people who had handled cardiovascular tablets. Lloyd (1986c) used HPLC/PMDE to detect glycerol dinitrates on handswabs from persons who had handled nitroglycerine (glycerol trinitrate). In discussing applications of HPLC/PMDE to analysis of explosives and organic gunshot residue, Lloyd (1986b, 1987) noted that HPLC/PMDE results were confirmed by GC/TEA.

Ruetter *et al.* (1983a) showed by before and after ion chromatography that evaporation of aqueous extracts of water gel explosives caused loss from solution of ammonium ion. By extension, this applies to ammonia dynamites and although Beveridge *et al.* (1975) showed that some residual ammonium nitrate can be recovered from acetone extracts of ammonia dynamites, analysis of aqueous extracts by IC before evaporation is clearly preferable when analyzing for presence of ammonium ion. Insoluble components are analyzed by such methods as IR, SEM/EDX and XRPD.

Cap-sensitive slurries (water gels): Slurry explosives utilize nitrate salts in water solution which enables the nitrate oxidizer to come into closer contact with the sensitizer/fuel than, for example, in dynamite. However, unlike emulsion explosives in which, by definition, the oxidizer and the fuel are both liquids, some of the oxidizer in the salt remains in the solid phase. The slurry formulations include thickeners and gelling agents to stabilize the liquid phase. Typical sensitizer/fuels are ethylene glycol mononitrate (EGMN) and monomethylamine nitrate (MMAN). Aluminum is a typical fuel. The primary oxidizer is ammonium nitrate but sodium and calcium nitrate frequently are included in the formulation.

Cap sensitive slurries or water gels consist of ammonium and other nitrates plus chemical sensitizers such as EGMN and MMAN. EGMN is analyzed in the same way as EGDN or NG and the nitrate salts are most conveniently analyzed by IC and SEM/EDX. If sufficient material is available, MMAN is readily identified by its infrared spectrum; otherwise its presence is best indicated by IC.

EGMN can readily be analyzed by GC/ECD (Canadian Industries Ltd., personal communication). Prime and Krebs (1984) used HPLC/UV to identify EGMN in post-blast residue and also successfully identified MMAN both unreacted and in post blast residue by HPLC/UV of its dansyl chloride derivative. Beveridge *et al.* (1983) identified MMAN in post blast residue from its IR spectrum (Parker 1975) and also recovered traces of unreacted ammonium nitrate, calcium, sodium and aluminum from various test explosions of slurries. Other methods used were SEM/EDX for elemental analysis and TLC and IR for nitrate. Unreacted calcium nitrate and MMAN were recovered in acetone as well as aqueous extracts. Peterson *et al.* (1983) derived TLC systems for analysis of alkyl ammonium nitrates. IC on unevaporated aqueous extracts, however, is the most practical method for detecting MMAN, since Ruetter and Buechele (1983) have reported that before and after IC showed that much of the ammonium and methylammonium ions were lost by evaporation of aqueous extracts of MMAN-containing water gels.

Cap-sensitive emulsions: The basic requirement of a detonating explosive is that an oxidizer and a fuel be in intimate contact and that they be sensitized by other explosive compounds or by physical mechanisms to produce hot spots. The primary emulsion oxidizer is ammonium nitrate and fuels typically are oils and waxes. A solid fuel such as aluminum can also be distributed within the emulsion. In dynamites, EGDN and NG are both sensitizers and fuels; in slurries, such compounds as EGMN and MMAN act as sensitizers and fuels; in both dynamites and slurries there are also voids (air bubbles) which act as sensitizers. In emulsions, the oxidizers and fuels are both in the liquid phase and so intimately mixed that voids are sufficient to sensitize them and they do not contain chemical sensitizers. Thus, an emulsion explosive is a water-in-oil emulsion containing voids in the form of air bubbles and/or glass microspheres.

Little forensic work has been reported on emulsions; but since the primary ingredients are AN, hydrocarbon oils and waxes, one scheme for analyzing unreacted explosive would be solvent extraction by pentane or ether to remove the hydrocarbons which can be analyzed by GC/FID and by water to remove the AN which can be identified by IC, IR etc.. There could be an insoluble residue of glass microspheres. In real-world residues, however, a lack of emulsion-specific components can make classification difficult and the inclusion in some formulations of perchlorate salts can make it excessively challenging.

VI - Some Less Common Explosives

Zitrin *et al.* (1983) have described the identification of two unusual explosives, triacetonetriperoxide (TATP) and hexamethylenetriperoxidediamine (HMTD) by systematic analysis using GC/MS under both EI and CI conditions, IR and nuclear magnetic resonance (NMR). Contemporaneously and equally successfully, Ruetter *et al.* (1983b) described identification of HMTD by systematic analysis using HPLC/UV/TEA, GC/MS under EI and CI conditions, IR, XRPD and NMR, and identified two major components of a no-headache dynamite made by the Hercules company - diethyleneglycol dinitrate (DEGDN) and metriol trinitrate (MTN; also known as 1,1,1 trimethylolethane trinitrate) by use of HPLC-UV-TEA.

SUMMARY

The fact that traces of volatile explosives can now be detected in grossly contaminated substrates five years after an explosion illustrates how the field of explosive analysis has advanced and continues to advance through communication and application of experimental results obtained by dedicated and often unsung researchers within our international community of forensic scientists. However, on rare occasions our collective efforts are publicly recognized. For instance, a recent editorial in the Vancouver Sun concerning the earlier cited case ended: "still, the best deterrent, in this as in all cases, will not be the severity of the sentence but the fact that Mr. Reyat was caught and convicted at all. For that, the forensic scientists and policemen in Canada and Japan all deserve our praise and thanks". Forensic scientists and policemen can ask for nothing more; but the key point is, of course, that such praise and thanks should extend to all scientists everywhere who have contributed to the advancement of the field.

REFERENCES

Amas, S. A. H. and Yallop, H. J. (1966). Identification of industrial explosives of the gelignite type, J. Foren. Sci. Soc. 6:185-188.

Amas, S. A. H. and Yallop, H. J. (1969). A Test for cyclotrimethylenetrinitramine, Analyst 94:828.

Archer, A. W. (1975). Separation and identification of minor components in smokeless powders by thin layer chromatography, J. Chrom. 108:401-404.

Basch, A., Margalit, Y., Abramovich-Bar, S., Bamberger, Y., Daphna, D., Tamiri, T. and Zitrin, S. (1986). Decomposition products of PETN in post-explosion analysis, J. Energetic Materials 4:77-91.

Bender, E. C. (1983). Analysis of smokeless powders by HPLC, In: Proceedings of the International Symposium on the Analysis and Detection of Explosives, National Technical Information Service, Springfield, VA, pp. 309-320.

Bender, E. C. (1986a). The analysis of dicyandiamide and sodium benzoate in pyrodex by HPLC, Crime Lab. Digest 16:76-77.

Bender, E. C. (1986b). Indirect photometric detection of anions for the analysis of low explosives, Crime Lab. Digest 16:78-83.

Berberich, D. W., Yost, R. A. and Fetterolf, D. D. (1988). Analysis of explosives by liquid chromatography/thermospray/mass spectrometry, J. Foren. Sci., 33:946-959.

Beveridge, A. D. (1986). Explosive residue analysis in the mid-1980s - an expanding and challenging role for the forensic scientist, J. Energetic Materials 4:29-75.

Beveridge, A. D., Greenlay, W. R. A. and Shaddick, R. C. (1983). Identification of reaction products in residues from explosives, In: Proceedings of the International Symposium on the Analysis and Detection of Explosives, National Technical Information Service, Springfield, VA, pp. 53-57.

Beveridge, A. D., Payton, S. F., Audette, R. J., Lambertus, A. J. and Shaddick, R. C. (1975). Systematic analysis of explosive residues, J. Foren. Sci. 20:431-454.

Collins, D. A. (1989). Modification to a thermal energy analyzer with associated electronic filtering for improved gas chromatographic analysis of explosives traces, J. Chrom. 483:379-383.

Conklin, J. A. (1981). Chemistry of fireworks, Chem. Eng. News, June:24-32.

Deak, J. S., Clark, H., Dagenais, C., Jones, S., McClure, D. and Richardson, B. W. (1989). Post-blast residue analysis in the RCMP laboratories, In: Proceedings

Third Symposium on Analysis and Detection of Explosives, Fraunhofer Institute fur Chemische und Technologie (ICT), Germany, pp. 18-1, pp. 18-19.

DeBruyne, P., Arijs, J. and DeBisschop, H. (1989). The HPLC determination of some propellant additives, In: Proceedings Third Symposium on Analysis and Detection of Explosives, Fraunhofer Institute fur Chemische und Technologie (ICT), Germany, pp. 27-1, pp. 27-15.

Douse, J. M. F. (1981). Trace analysis of explosives at the low picogram level by silica capillary gas-liquid chromatography with electron capture detection, J. Chrom. 208:83-88.

Douse, J. M. F. (1982). Trace analysis of explosives in handswab extracts using amberlite XAD-7 porous polymer beads, silica capillary column gas chromatography with electron-capture detection and thin layer chromatography, J. Chrom. 234:415-425.

Douse, J. M. F. (1983). Trace analysis at the low picogram level using silica capillary column gas chromatography with thermal energy analyzer detection, J. Chrom. 256:359-362.

Douse, J. M. F. (1985). Trace analysis of explosives at the low nanogram level,in handswab extracts using columns of Amberlite XAD-7 porous polymer beads and silica capillary gas chromatography with thermal energy analysis and electron capture detection, J. Chrom. 328:155-165.

Douse, J. M. F. (1987). Improved method for the trace analysis of explosives by silica capillary column gas chromatography with thermal energy analysis detection, J. Chrom. 410:181-189.

Douse, J. M. F. (1988). Trace analysis of explosives by capillary supercritical fluid chromatography with thermal energy analysis detection, J. Chrom. 445:244-250.

Douse, J. M. F. and Smith, R. N. (1986). Trace analysis of explosives and firearm discharge residues in the Metropolitan Police Forensic Science Laboratory, J. Energetic Materials 4:169-186.

Encyclopedia of Explosives and Related Items, Vols 1 to 10. US Army Research and Development Command, Dover, N. J. (National Technical Information Service, Springfield, VA).

Fine, D. H., Yu, W. C., Goff, E. U., Bender, E. C. and Reutter, D. J. (1984). Picogram analysis of explosive residues using the thermal energy analyzer (TEA), J. Foren. Sci. 29:732-746.

Fung, T. (1986). Identification of two unusual pipe bomb fillers, Can. Soc. Foren. Sci. J. 18:222-226.

Garner, D. D., Fultz, M. L. and Byall, E. B. (1986). The ATF approach to post-blast explosives detection and identification, J. Energetic Materials 4:133-148.

Glattstein, B. and Kraus, S. (1986). Determination of oxidizing anions in explosive mixtures by phase transfer, J. Energetic Materials 4:149-157.

Goff, E. U., Yu, W. C. and Fine, D. H. (1983). Description of a nitro/nitroso specific detector for the trace analysis of explosives, In: Proceedings of the International Symposium on the Analysis and Detection of Explosives, National Technical Information Service, Springfield, VA, pp. 159 - 168.

Green, M. U. (1986). Ion chromatography analysis of perchlorate in percholorate/sugar explosive devices, Liquid Chrom. Magazine 3:894.

Jane, I., Brookes, P.G., Douse J. M. F. and O'Callaghan, K. A. (1983). Detection of gunshot residues via analysis of their organic constituents, In: Proceedings of the International Symposium on the Analysis and Detection of Explosives, National Technical Information Service, Springfield, VA, pp. 475-483.

Jenkins, R. and Yallop, H. J. (1970). The identification of explosives in trace quantities on objects near an explosion, Explosivstoffe 6:139-141.

Kee, T. G., Holmes, D. M., Doolan, K., Hamill, J. A. and Griffin, R. M. E. (1990). The identification of individual propellant particles, J. Foren. Sci. Soc. 30:285-292.

Keto, R. O. (1986). Improved method for the analysis of the military explosive composition C4, J. Foren. Sci. 31:241-249.

Keto, R. O. (1989a). Comparison of smokeless powders by pyrolysis capillary gas chromatography and pattern recognition, J. Foren. Sci. 34:74-82.

Keto, R. O. (1989b). Analysis of the eastern bloc explosive Semtex-H, In: Proceedings Third Symposium on Analysis and Detection of Explosives, Fraunhofer Institute fur Chemische und Technologie (ICT), Germany, pp. 11-1, pp. 11-20.

Krull, I. (1983). HPLC analysis of explosives and related materials, In: High Performance Liquid Chromatography in Forensic Chemistry (Lurie, I. S. and Wittwer, J. D., eds.). Marcel Dekker, Inc., NY, pp. 357-398.

Lloyd, J. B. F. (1983a). High performance liquid chromatography of organic explosives components with electrochemical detection at a pendant mercury drop electrode, J. Chrom. 257:227-236.

Lloyd, J. B. F. (1983b). Transfer of nitroglycerin from cardiovascular tablets to hands, J. Foren. Sci. Soc. 23:307-311.

Lloyd, J. B. F. (1983c). Clean-up procedures for the examination of swabs for explosives traces by high performance liquid chromatography with electrochemical detection at a pendant mercury drop electrode, J. Chrom. 261:391-406.

Lloyd, J. B. F. (1984). Detection and differentiation of nitrocellulose traces of forensic science interest with reductive mode electrochemical detection at a pendent mercury drop electrode coupled with size exclusion chromatography, Anal. Chem. 56:1907-1912.

Lloyd, J. B. F. (1985a). Adsorption characteristics of organic explosives compounds typically used in clean-up and related trace analysis techniques, J. Chrom. 328:145-154.

Lloyd, J. B. F. (1985b). Microcolumn clean-up and recovery techniques for organic explosives compounds and for propellants traces in firearms discharge residues, J. Chrom. 330:121-129.

Lloyd, J. B. F. (1986a). Glyceryl dinitrates in the detection of skin-contact with explosives and related materials of forensic science interest, J. Foren. Sci. Soc. 26:341-348.

Lloyd, J. B. F. (1986b). Liquid chromatography of firearms propellants traces, J. Energetic Materials 4:239-271.

Lloyd, J. B. F. (1986c). Adsorption and exclusion characteristics of nitrocellulose with reference to a microcolumn clean-up technique for the detection of propellants traces in firearms discharge residues, J. Chrom. 351:323-330.

Lloyd, J. B. F. (1987). Liquid chromatography with electrochemical detection of explosives and firearms propellant traces, Anal. Proc. 24:239-240.

Lloyd, J. B. F. and King, P. M. (1989). Detection and persistence of Semtex and some other explosives on skin surfaces, In: Proceedings Third Symposium on Analysis and Detection of Explosives, Fraunhofer Institute fur Chemische und Technologie (ICT), Germany, pp. 9-1, pp. 9-14.

Lloyd, J. B. F. and King, R. M. (1990). One-pot processing of swabs for organic explosives and firearms residue traces, J. Foren. Sci. 35:956-959.

Mach, M. H., Pallos, A. and Jones, P. F. (1978). Feasibility of gunshot residue detection via its organic constituents. Part 1: Analysis of smokeless powders by combined gas chromatography-chemical ionization mass spectrometry, J. Foren. Sci. 23:433-444.

McLuckey, S. A., Glish, G. L. and Carter, J. A. (1985). The analysis of explosives by tandem mass spectrometry, J. Foren. Sci. 30:773-788.

Meyers, R. E. (1978). A systematic approach to the forensic examination of flash powders, J. Foren. Sci. 23:66-73

Midkiff, C. R. (1989). Identification and characterization of flashpowders, In: Proceedings Third Symposium on Analysis and Detection of Explosives, Fraunhofer Institute fur Chemische und Technologie (ICT), Germany, pp. 17-1, pp. 17-17.

Midkiff, C. R. and Washington, W. D. (1974). Systematic approach to the detection of explosive residues III Commercial; dynamite, J. Ass. Off. Anal. Chem. 57:1092-1097.

Nowicki, J. and Pauling, S. (1988). Identification of sugars in explosive residues by gas chromatography-mass spectrometry, J. Foren. Sci. 33:1254-1261.

Parker, R. G. (1975). Analysis of explosives and explosive residues. part 3: Monomethylamine nitrate, J. Foren. Sci. 20:257-260.

Penton, Z. (1983). Determination of nitro explosives by GC utilizing an on-column capillary injector, In: Proceedings of the International Symposium on the Analysis and Detection of Explosives, National Technical Information Service, Springfield, VA, pp. 123-128.

Peterson, G. F., Dietz, W. R. and Stewart, L. E. (1983). Identification of explosives containing alkylammonium nitrates by thin layer chromatography, J. Foren. Sci. 28:638-643.

Prime, R. J. and Krebs, J. (1980). The recovery and identification of ethyleneglycoldinitrate and nitroglycerine in explosion debris using preconcentration and high performance liquid chromatography, Can. Soc. Foren. Sci. J. 13:27-34.

Prime, R. J. and Krebs, J. (1984). The analysis of ethyleneglycolmononitrate and monomethylamine nitrate from commercial blasting agents in post blast samples, Can. Soc. Foren. Sci. J. 17:35-40.

Propellant Profiles (1988). 2nd Edition. Wolfe Publishing Co. Inc., Prescott, AZ.

Rudolph, T. L. (1983). The characterization of some low explosive residues by ion chromatography, In: Proceedings of the International Symposium on the Analysis and Detection of Explosives, National Technical Information Service, Springfield, VA, pp. 213-219.

Rudolph, T. L. and Bender, E. C. (1983). A scheme for the analysis of explosive residues, In: Proceedings of the International Symposium on the Analysis and Detection of Explosives, National Technical Information Service, Springfield, VA, pp. 71-78.

Ruetter, D. J. and Buechele, R. C. (1983). Ion chromatography of explosives and explosive residues, In: Proceedings of the International Symposium on the Analysis and Detection of Explosives, National Technical Information Service, Springfield, VA, pp. 199-207.

Ruetter, D. J., Buechele, R. C. and Rudolph, T. L. (1983a). Ion chromatography in bombing investigations, Anal. Chem. 55:1468A-1472A.

Ruetter, D. J., Bender, E. C. and Rudolph, T. L. (1983b). Analysis of an unusual explosive: methods used and conclusions drawn from two cases, In: Proceedings of the International Symposium on the Analysis and Detection of Explosives, National Technical Information Service, Springfield, VA, pp. 149-158.

Selavka, C. M., Tontarski, R. E. and Strobel, R. A. (1988). Improved determination of nitrotoluenes using liquid chromatography and photolytically assisted thermal energy analysis (LC-PAT), J. Foren. Sci. 32:941-952.

Skelly, N. E. (1982). Separation of inorganic and organic anions on reversed-phase liquid chromatography columns, Anal. Chem. 54:712-715.

Tamiri, T. and Zitrin, S. (1986). Capillary column gas chromatography/mass spectrometry of explosives, J. Energetic Materials 4:215-238.

Tardif, H. P. and Sterling, T. S. (1967). Explosively produced fractures and fragments in forensic investigations, J. Foren. Sci. 12:247-271.

Twibell, J. D., Home, J. M., Smalldon, K. W., Higgs, D. G. and Hayes, T. S. (1982). Assessment of solvents for the recovery of nitroglycerine from hands using cotton swabs, J. Foren. Sci. 27:792-800.

Twibell, J. D., Turner, S. L., Smalldon, K. W. and Higgs D. G. (1984). The persistence of military explosives on hands, J. Foren. Sci. 29:284-290.

Urbanski, T. (1964, 1965, 1967, 1984). Chemistry and Technology of Explosives Vols. 1 to 4. Pergamon Press Ltd., NY.

Urbanski, T. and Vasudeva, S. K. (1981). Explosions and explosives: fundamental aspects, J. Sci. Indust. Res. 40:512-519.

Voyksner, R. D. and Yinon, J. (1986). Trace analysis of explosives by thermospray high-performance liquid chromatography-mass spectrometry, J. Chrom. 354:393-405.

Wardleworth, D. F. and Ancient, S. A. (1983). A novel method for the recovery of volatile explosive traces, In: Proceedings of the International Symposium on the Analysis and Detection of Explosives, National Technical Information Service, Springfield, VA, pp. 405-408.

Washington, W. D. and Midkiff, C. R. (1986). Explosive residues in bomb-scene investigations; new technology applied to their detection and identification, In: Forensic Science (Davies, G., ed.). American Chemical Society, Washington, D. C., pp. 259-278.

Woolfson-Bartfeld, D., Grushka, E., Abramovich-Bar, S. and Bamberger, Y. (1989). Proceedings Third Symposium on Analysis and Detection of Explosives, Fraunhofer Institute fur Chemische und Technologie (ICT), Germany, pp. 19-1, pp. 19-14.

Yinon, J. (1982). Mass spectrometry of explosives: nitro compounds, nitrate esters, and nitramines, Mass Spectrometry Reviews 1:257-307.

Yinon, J. (1987). Mass spectrometry of explosives, In: Forensic Mass Spectrometry (Yinon, J., ed.). CRC Press, Inc., Boca Raton, FL, ch. 4, pp. 105-130.

Yinon, J. (1988). Identification of explosives' mixtures by tandem mass spectrometry (MS/MS), Can. Soc. Foren. Sci. J. 21:46-53.

Yinon, J. and Hwang, D.-G. (1983). High-performance liquid chromatography-mass spectrometry of explosives, J. Chrom. 268:45-53.

Yinon, J. and Zitrin, S. (1981). The Analysis of Explosives. Pergamon Press, NY.

Zitrin, S. (1986). Post explosion analysis of explosives by mass spectrometric methods, J. Energetic Materials 4:199-214.

Zitrin, S., Kraus, S. and Glattstein, B. (1983). Identification of two rare explosives, In: Proceedings of the International Symposium on the Analysis and Detection of Explosives, National Technical Information Service, Springfield, VA, pp. 137-141.

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ANALYTICAL PYROLYSIS: AN OVERVIEW WITH FORENSIC APPLICATIONS

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Pyrolysis, simply put, is the breaking apart of chemical bonds by the use of thermal energy only. Analytical pyrolysis is the technique of studying molecules either by observing their behavior during pyrolysis or by studying the resulting molecular fragments. The analysis of these processes and fragments tells us much about the nature and identity of the original larger molecule. The production of a variety of smaller molecules from some larger original molecule has fostered the use of pyrolysis as a sample preparation technique, extending the applicability of instrumentation designed for the analysis of gaseous species to solids, and especially polymeric materials. As a result, gas chromatography, mass spectrometry and Fourier-transform infrared spectrometry may be used routinely for the analysis of samples such as synthetic polymers, biopolymers, composites and complex industrial materials.

The fragmentation which occurs during pyrolysis is analogous to the processes which occur during the production of a mass spectrum. Energy is put into the system, and as a result, the molecule breaks apart into stable fragments. If the energy parameters (temperature, heating rate and time) are controlled in a reproducible way, the fragmentation is characteristic of the original molecule, based on the relative strengths of the bonds between its atoms. The same distribution of smaller molecules will be produced each time an identical sample is heated in the same manner, and the resulting fragments carry with them much information concerning the arrangement of the original macromolecule.

The application of pyrolysis techniques to the study of complex molecular systems covers a wide and diversified field. Several books have been published which present theoretical as well as practical aspects of the field, including a good introductory text by Irwin (1982) and a compilation of gas chromatographic applications by Liebman and Levy (1985). A recent bibliography (Wampler 1989a) lists approximately 500 recent papers in areas as diverse as food, environmental and geochemical analysis, while the application to microorganisms has been examined by Morgan *et al.* (1990). Additional references and specific analyses will be discussed in the applications section of this paper.

DEGRADATION MECHANISMS

The degradation of a molecule which occurs during pyrolysis is caused by the dissociation of a chemical bond and the production of free radicals. The general processes employed to explain the behavior of these molecules are based on free radical degradation mechanisms. The way in which a molecule fragments during pyrolysis, and the identity of the fragments produced, depend on the types of chemical bonds involved, and on the stability of the resulting smaller molecules. If the subject molecule is based on a carbon chain backbone, such as that found in many synthetic polymers, it may be expected that the chain will break apart in a fairly random fashion to produce smaller molecules chemically similar to the parent molecule. Some of the larger fragments produced will preserve intact structural information snipped out of the polymer chain, and the kinds and relative abundances of these specific smaller molecules give direct evidence of macromolecular structure.

RANDOM SCISSION

Breaking apart a long chain molecule such as the carbon backbone of a synthetic polymer into a distribution of smaller molecules is referred to as random scission. If all of the C-C bonds are of about the same strength, there is no reason for one to break more than another, and consequently the polymer fragments to produce a wide array of smaller molecules. The polyolefins are good examples of materials which behave in this manner. When poly(ethylene) (shown as Structure I with hydrogen atoms left off for simplicity) is heated sufficiently to cause pyrolysis, it breaks apart into hydrocarbons which may contain any number of carbons, including methane, ethane, propane and so on. Chain scission produces hydrocarbons with terminal free radicals (structure II), which may be

$$\begin{array}{ll} \text{I} & -C-C-C-C-C-C- \\ & \qquad\quad\;\downarrow \\ \text{II} & -C-C-C\cdot \quad \cdot C-C-C- \end{array}$$

stabilized in several ways. If the free radical abstracts a hydrogen atom from a neighboring molecule, it becomes a saturated end, and creates another free radical in the neighboring molecule (structure III) which itself may stabilize in a number of ways. The most likely of these is beta-scission, which accounts for most of the polymer backbone degradation by producing an unsaturated end and a new terminal free radical. This process continues,

$$\text{III}\qquad \text{-C - C -}\overset{\curvearrowright}{\dot{\text{C}}}\cdot\text{C}\,\vdots\,\text{- C - C-}$$

$$\downarrow \text{Beta-scission}$$

$$\text{IV}\qquad \text{-C - C - C} = \text{CH}_2 + \cdot\text{C - C-}$$

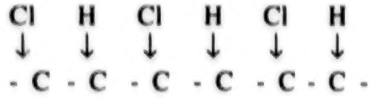
producing hydrocarbon molecules which are saturated, have one terminal double bond, or a double bond at each end. When analyzed by gas chromatography, the resulting pyrolysate looks like the bottom chromatogram in Figure 1. Each triplet of peaks represents the diene, alkene and alkane containing a specific number of carbons and eluting in that order. The next set of three peaks contain one more carbon, and so on. It is typical to see all chain lengths from methane to compounds containing 35 to 40 carbons, limited only by the upper temperature of the GC column.

When poly(propylene) is pyrolyzed, it behaves in much the same manner, producing a series of hydrocarbons which have methyl branches indicative of the structure of the original polymer. The center pyrogram in Figure 1 shows poly(propylene), revealing again a recurring pattern of peaks, with each group now containing three more carbons than the preceding. Likewise, when a polymer made from a four carbon monomer such as isobutylene is pyrolyzed, it produces yet another pattern of peaks, with oligomers differing by four carbons, as seen in the top pyrogram in Figure 1. The relationships of specific compounds produced in the pyrolysate to the original polymer structure have been extensively studied, by Tsuge *et al.* (1980) for example in the case of poly(propylenes) as well as the effects of temperature and heating rate (Wampler 1989b).

SIDE GROUP SCISSION

When poly(vinyl chloride) is pyrolyzed, no such oligomeric pattern occurs. Instead of undergoing random scission to produce chlorinated hydrocarbons, PVC produces aromatics, especially benzene, toluene and naphthalene, as shown in Figure 2. This is the result of a two-step degradation mechanism which begins with the elimination of HCl from the polymer chain (structure V), leaving the poly-unsaturated backbone shown as structure VI.

V



$$\text{- }\overset{\text{Cl}}{\overset{\downarrow}{\text{C}}}\text{ - }\overset{\text{H}}{\overset{\downarrow}{\text{C}}}\text{ - }\overset{\text{Cl}}{\overset{\downarrow}{\text{C}}}\text{ - }\overset{\text{H}}{\overset{\downarrow}{\text{C}}}\text{ - }\overset{\text{Cl}}{\overset{\downarrow}{\text{C}}}\text{ - }\overset{\text{H}}{\overset{\downarrow}{\text{C}}}\text{ -}$$

$$\downarrow \text{- HCl}$$

$$\text{VI}\qquad \text{-C} = \text{C - C} = \text{C - C} = \text{C-}$$

Upon further heating, this unsaturated backbone produces the characteristic aromatics seen in the pyrogram. This mechanism has been well characterized, and the occurrence of chlorinated aromatics used as an indication of polymer defect structures, as in the work of Lattimer and Kroenke (1980).

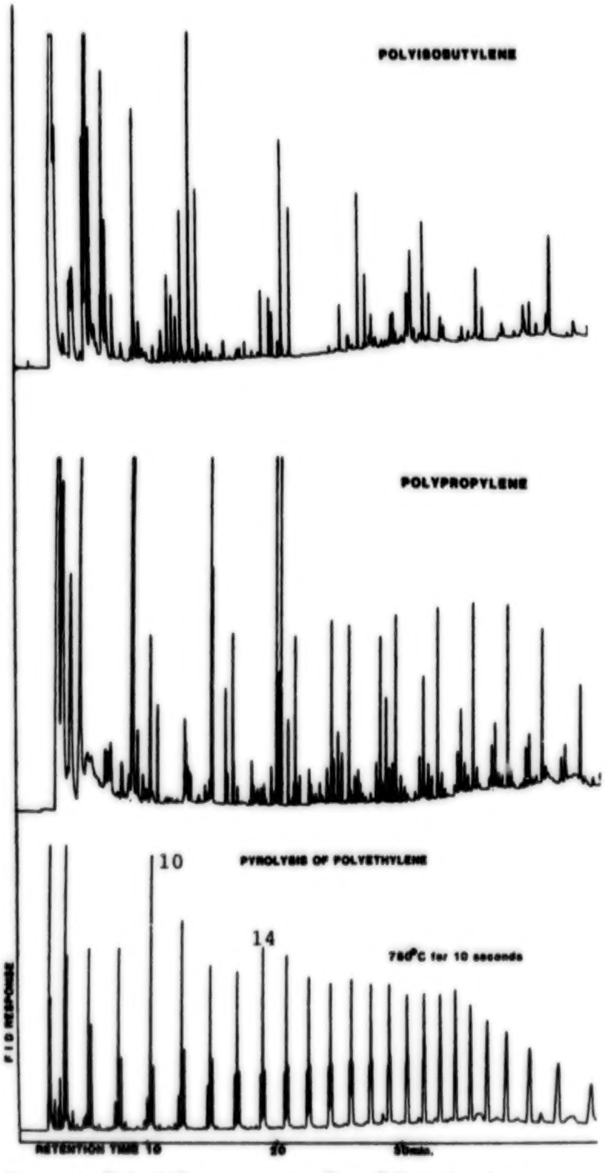


Figure 1. Polyolefin pyrograms. Top: Poly(isobutylene), center: Poly(propylene), bottom: Poly(ethylene).

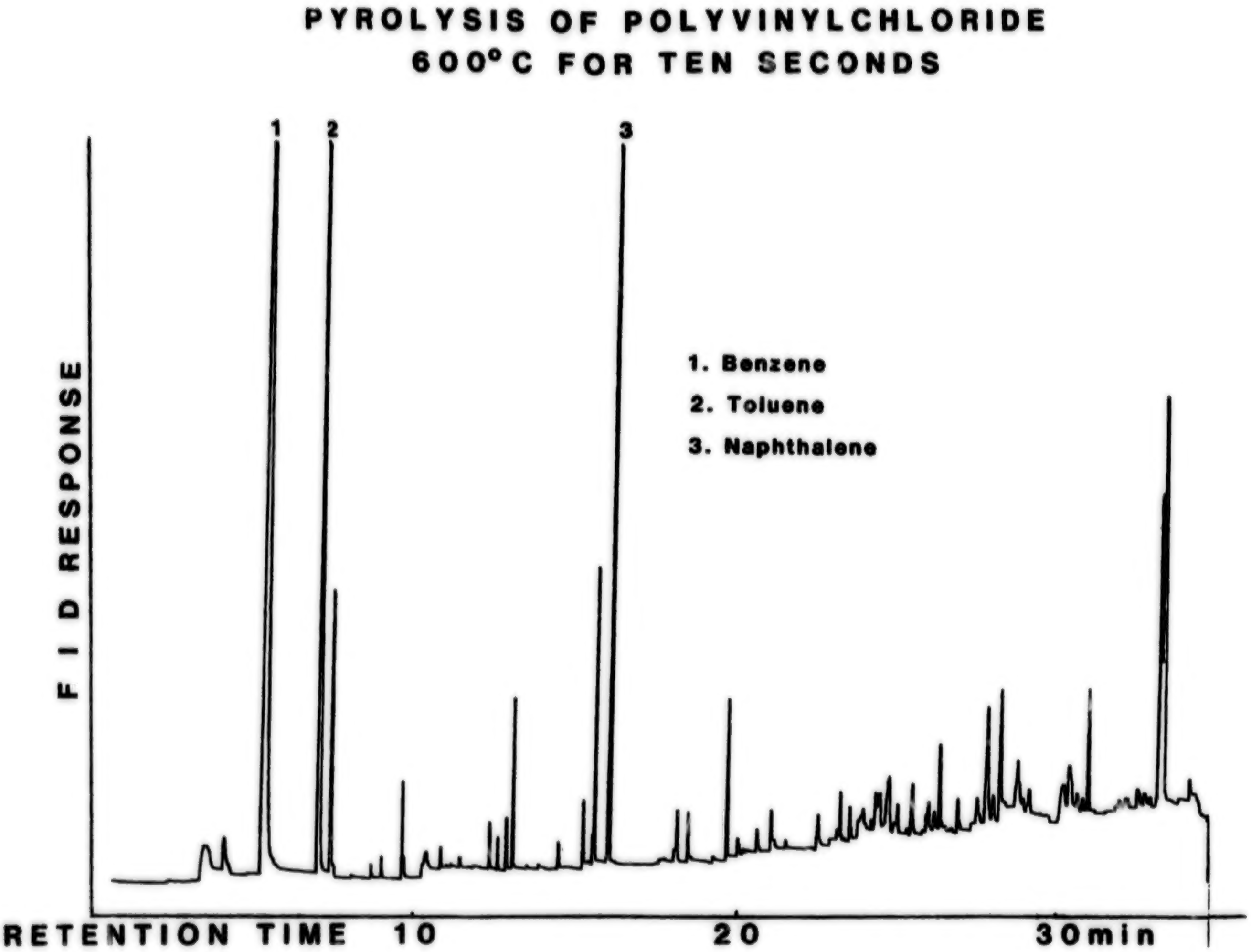
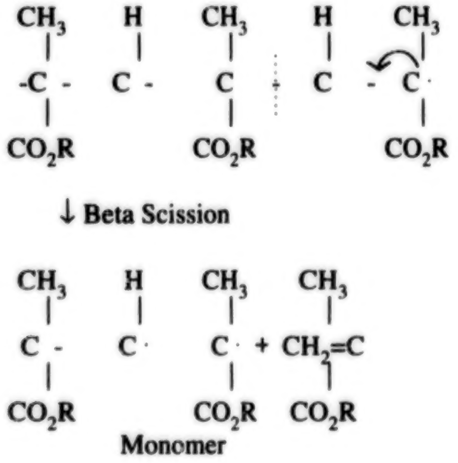


Figure 2. Pyrogram of Poly(vinyl chloride).

MONOMER REVERSION

A third pyrolysis behavior is evidenced by polymers such as poly(methyl methacrylate). Because of the structure of methacrylate polymers (structure VII), the favored degradation is

VII



$$\begin{array}{ccccccccc} CH_3 & & H & & CH_3 & & H & & CH_3 \\ | & & | & & | & & | & & | \\ -C & - & C & - & C & \vdots & C & - & C\cdot \\ | & & & & | & & & & | \\ CO_2R & & & & CO_2R & & & & CO_2R \end{array}$$

$$\downarrow \text{Beta Scission}$$

$$\begin{array}{cccccc} CH_3 & & H & CH_3 & & CH_3 \\ | & & | & | & & | \\ C & - & C\cdot & C\cdot & + & CH_2=C \\ | & & & | & & | \\ CO_2R & & & CO_2R & & CO_2R \\ & & & & & \text{Monomer} \end{array}$$

essentially a reversion to the monomer. Monomer production is for the most part unaffected by the R group, so that poly(methyl methacrylate) will revert to methyl methacrylate, poly(ethyl methacrylate) will produce ethyl methacrylate, and so on. This proceeds in copolymers as well, with the production of both monomers in roughly the original polymerization ratio. Figure 3 shows a pyrogram of poly(ethyl methacrylate), with the ethyl methacrylate monomer peak by far the predominant product. A pyrogram of a copolymer of two or more methacrylate monomers would contain a peak for each of the monomers in the polymer.

RELATIVE BOND STRENGTHS

The question of which degradation mechanism a particular polymer will be subjected to - Random Scission, Side Group Scission or Monomer Reversion, or a combination of these - is simplified by considering the nature of thermal degradation as a free radical process. All of the degradation products shown above, as well as

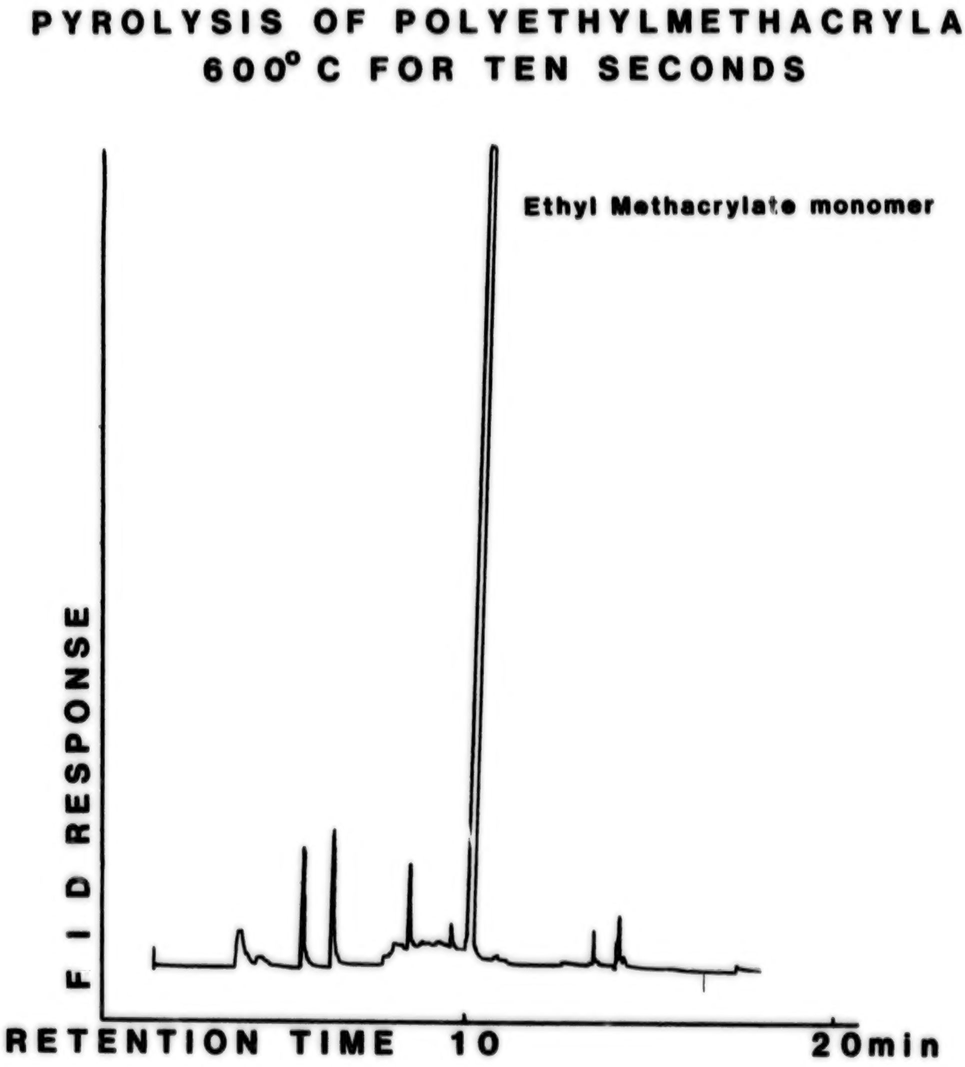


Figure 3. Pyrogram of Poly(ethyl methacrylate).

minor constituents, and deviations to the simplified rules are consistent with the following general statements:

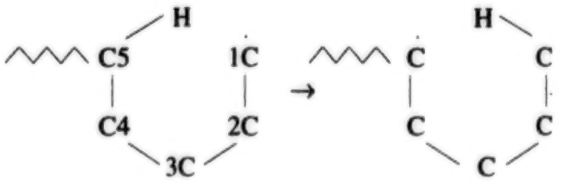
Pyrolysis degradation mechanisms are free radical processes and are initiated by breaking the weakest bonds first;

The composition of the pyrolysate will be based on the stability of the free radicals involved and on the stabilities of the product molecules.

Free radical stability follows the usual order of $3^\circ > 2^\circ > 1^\circ > CH_3$, and intramolecular rearrangements which produce more stable free radicals play an important role, particularly the shift of a hydrogen atom. A quick review of the previous degradation examples will help show how each of the above categories is in reality just one aspect of the general rule of free radical processes.

Polyolefins

Poly(ethylene) and the other polyolefins contain only C-C bonds and C-H bonds. Since an average C-C bond is about 83 Kcal/mole and a C-H bond 94 Kcal/mole, the initiation step involves breaking the backbone of the molecule, with subsequent stabilization of the free radical. The original free radicals formed are terminal or primary. Hydrogen abstraction from a neighboring molecule creates a C-H bond (stable product) and a new, secondary free radical, which may then undergo beta scission to form an unsaturated end. In addition, transfer of a hydrogen atom from the carbon 5 removed from the free radical (via a 6 membered ring) transforms a primary free radical to a secondary, increasing the free radical



stability. This new secondary free radical will either undergo beta scission or another 1-5 H shift. This stabilization by 1-5 hydrogen shifting explains the increased abundance of products in the pyrolysate of poly(ethylene) containing 6, 10, and 14 carbons (see again Figure 1 in which 10 and 14 carbon species are marked).

Vinyl Polymers

Poly(vinyl chloride) contains C-C, C-H and C-Cl bonds, with the C-Cl bonds weakest at about 73 Kcal/mole. Consequently, the first step is the loss of Cl which subsequently combines with hydrogen to form HCl, leaving the unsaturated polymer backbone, with formation of the very stable aromatic products upon further heating.

Methacrylates

Carbons in the chain of a methacrylate polymer are bonded to the CO_2R side group, the CH_3 side group, to hydrogens and to other chain carbons (structure VII), with C-C bonds being weaker than C-H bonds. Of the C-C bonds, the ones making up the chain are the weakest and produce the most stable free radicals, since breaking $C\text{-}CH_3$ produces CH_3., the least stable free radical. Consequently, beta-scission with unzipping back to monomer represents the most stable product formed by the most stable free radical.

APPLICATIONS

The application of pyrolysis techniques to the study of forensic samples has a long and well documented history, including a review of pyrolysis-mass spectrometry as a forensic tool in 1977 by Saferstein and Manura, and a general review by Wheals (1981). A wide variety of sample types has been investigated, including chewing gum, rubber and plastic parts from automobiles, drugs and bloodstains. The applications shown here will include examples from the more typical categories of paint analysis, fiber and document investigation, and a final section on the analysis of art materials.

Paint Analysis

Perhaps the best known forensic application of pyrolysis is the analysis of paint flakes from automobiles, a standard practice in many laboratories backed by substantial libraries of pyrograms and sample materials. Munson *et al.* (1985) describe their work using pyrolysis-capillary GC-MS for the analysis of paint samples, and Fukuda (1985) has published results on nearly 80 paints used in the Japanese automobile industry. The same techniques may be applied to paint samples recovered from non-automotive sources, including house paints, tool and machine coatings as well as varnishes from furniture and musical instruments.

Most automotive finishes are applied in layers, which may be removed selectively and analyzed individually, or pyrolyzed intact. An advantage provided by pyrolysis is that the inorganic pigment material is left behind and only the organic pyrolysate transferred to the analytical instrument. Because of the great variety of polymeric materials used as paints and coatings, including acrylics, urethanes, styrenes, epoxies etc., the resulting pyrograms may be quite complex. It is not always necessary to identify all of the constituents involved, however, to make comparisons among related paints. Figure 4 shows a comparison of three paint samples of similar monomer composition. Although many of the peaks are very similar for all three formulations, the inversion on the relative peak height in the second and third largest peaks makes it relatively straightforward to see that paints A and B are the same formulation and paint C is not a match.

Frequently samples like paint flakes present a problem to the analytical lab because they are small, non-volatile and opaque with inorganic pigments. Since pyrolysis prepares a volatile organic sample from a polymer or composite, it offers the ability to introduce these organics to an analytical instrument separate from the inorganics, using only a few micrograms of sample. This extends the use of analytical techniques such as mass spectrometry and FT-IR spectroscopy to the investigation of small complex samples. When an opaque paint is pyrolyzed, the organic constituents are volatilized and available for analysis apart from the pigment material. A paint formulation based on methacrylate monomers, for example, will pyrolyze to reveal the methacrylates despite the presence of the pigment, and techniques such as FT-IR which were previously unable to provide good spectral information, may be applied to the pyrolysate only. Figure 5 shows the pyrolysis-FT-IR comparison of poly(methyl methacrylate) and poly(ethyl methacrylate). In each case, a 200 µg sample of the solid polymer was pyrolyzed for 5 seconds in a cell fitted directly into the sample compartment of the FT-IR. The cell was positioned so that the FT-IR beam passed directly over the platinum filament of the pyrolyzer. The samples were pyrolyzed, and the pyrolysate scanned for 10 seconds, producing the spectra shown. This system, details of which are published (Washall and Wampler 1991) permits the rapid scanning of polymer based materials, requiring approximately one minute per sample.

Fibers and Textiles

Almost all clothing is made from fibers of natural polymers such a the proteins in silk and wool, and cellulose in cotton, synthetic polymers including the various

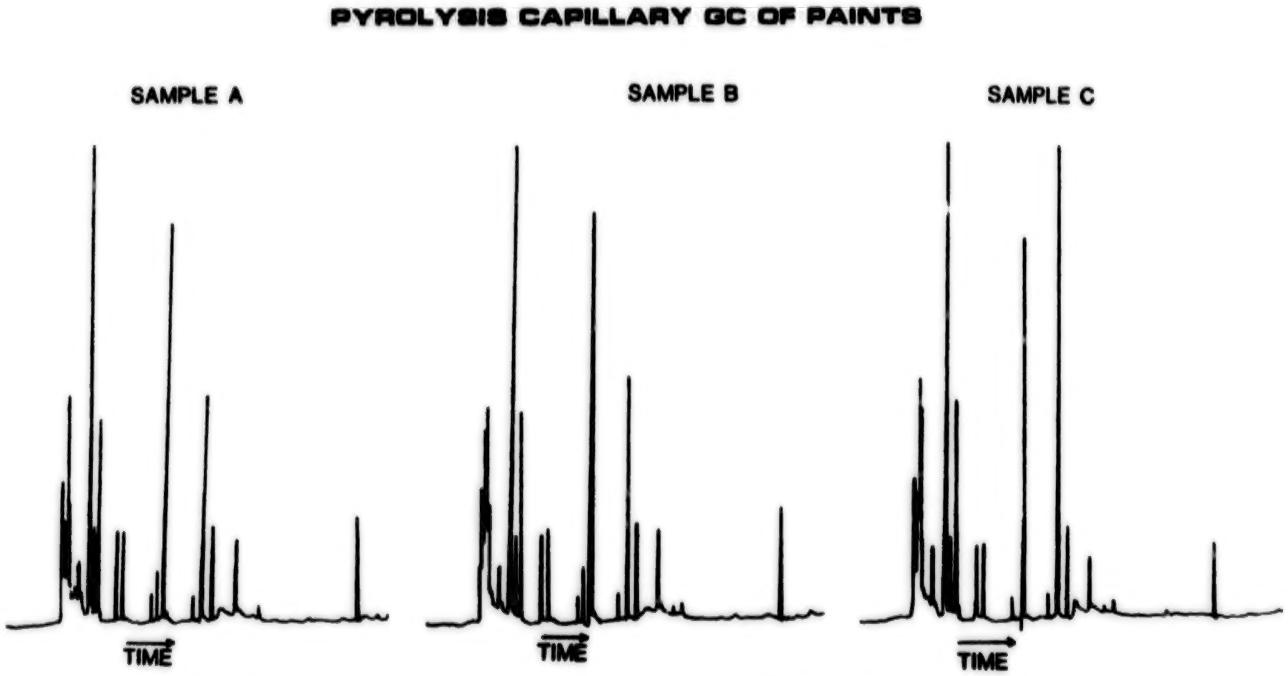


Figure 4. Comparison of paint pyrolyses, showing paints A and B matching, C being a different formulation.

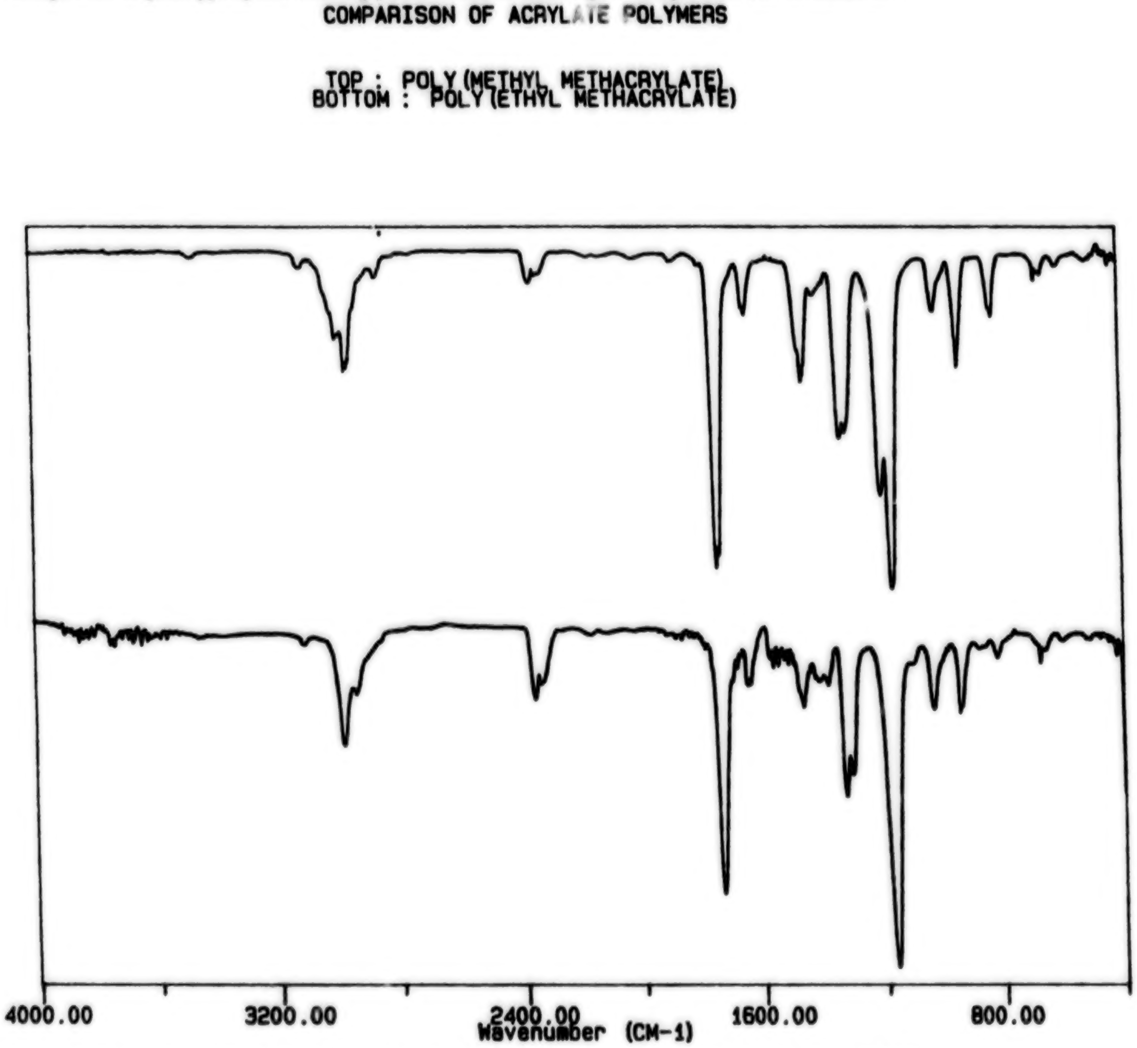


Figure 5. Comparison of Poly(methyl methacrylate) and Poly(ethyl methacrylate) by Pyrolysis-FT-IR.

nylons and polyesters, or blends of both natural and synthetic polymers. Since these polymers are all chemically different, the pyrolysates they generate are all distinctive and provide a ready means of fiber analysis. Significant work has been done in the analysis and comparison of the various nylons, by Tsuge *et al.* (1982) among others, as well as acrylate and methacrylate/acrylonitrile copolymer fibers by Saglam (1986). A good overview of fiber analysis by pyrolysis-MS was published by Hughes *et al.* (1978).

Figure 6 shows a pyrogram of silk fibers which are made of the protein fibroin, which is nearly 50% glycene. Figure 7 is a pyrogram of the polyamide nylon 6/12, which is formulated using a diamine containing 6 carbons and a dicarboxylic acid containing 12 carbons. Although both silk and nylon are polyamides, the chemical differences between them make distinctions using pyrolysis gas chromatography relatively simple. The same techniques may be used to differentiate among the various nylon formulations, to distinguish silk from wool, and so on.

Polymer blends used in clothing may be analyzed in the same manner. Because the degradation of a specific polymer is largely an intramolecular event, the presence of two different fibers being pyrolyzed simultaneously generally produces a pyrogram resembling the superimposition of the pyrograms of the two pure materials. A good example of this is shown in Figure 8, which compares pyrograms of cotton, polyester and cotton/polyester blend threads. Each sample was a piece of thread 1 cm in length, pyrolyzed at 750°C. The top pyrogram shows just cotton, which produces large amounts of CO_2 and H_2O, as well as some larger molecules which appear in the chromatogram. The bottom pyrogram is of polyester only, which produces a larger abundance of chromatographic peaks. The center pyrogram is the result of pyrolyzing a 50/50 cotton/polyester blend thread. Even though the cellulose and polyester are copyrolyzed, the patterns of each individually are easily discernable. Specific peaks are marked C for cotton and P for polyester, indicating peaks associated only with the pure material. Washall and Wampler (1989) have published further examples of pyrograms of complex, multicomponent systems.

Documents

Although much of the investigation of a written or printed document is conducted by handwriting specialists and microscopists, much about the chemical nature of the paper and inks involved in making the actual document may be revealed using pyrolysis. Zimmerman *et al.* (1986) used pyrolysis GC to extend the specificity of toner identification in photocopies. Ball-point pen ink, various papers and photocopy toners have been analyzed using a combination of headspace sampling and pyrolysis by Wampler and Levy (1987)

Photocopy toner materials are generally complex formulations of pigments and polymers unique to a spe-

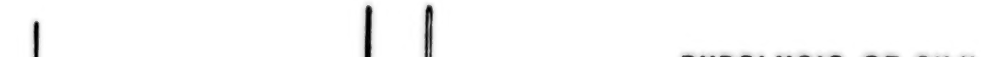


Figure 6. Pyrolysis of silk thread.

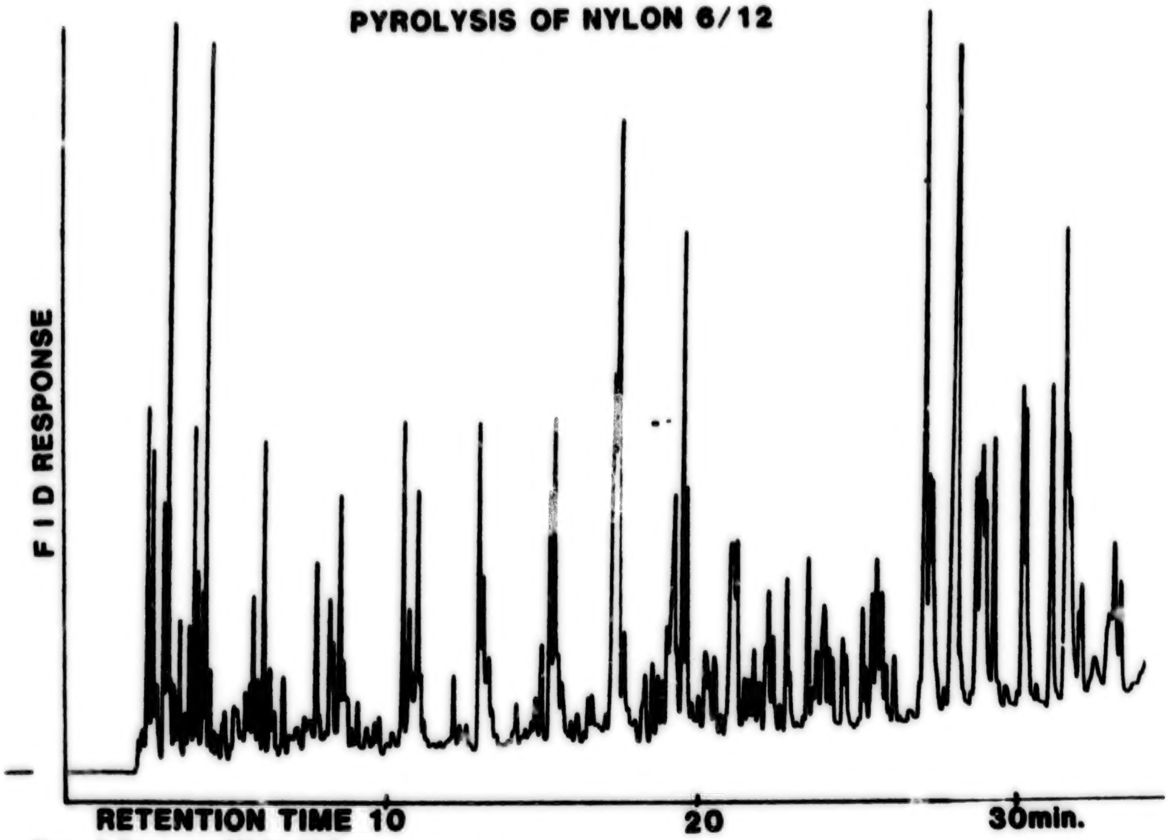


Figure 7. Pyrogram of Nylon 6/12.

cific manufacturer. The formulations of these toners frequently include poly(styrene), polyesters, acrylic polymers, methacrylic polymers of various side chain lengths and various other additives. The formulations vary both from manufacturer to manufacturer and also year to year as improvements are made and new processes introduced. Figure 9 shows a comparison of a Kodak and a Xerox photocopy made in 1985. The pyrograms were prepared by pyrolyzing a single letter punched from each photocopy. The punch, both paper and toner letter, was pyrolyzed at 650°C in a small quartz tube, and analyzed by capillary gas chromatography. The paper, which is essentially cellulose and produces a pyrogram like the one shown for cotton thread in Figure 8, contributes many of the smaller peaks, including the one marked G, which is furfural. The synthetic polymers in the toner materials pyrolyze to generate the larger peaks, including A, methyl methacrylate, and J, which is styrene.

When the same analysis is carrier out using a sample of paper which was written upon with ball-point pen, three sets of peaks are produced. Because the ink was applied as a fluid, there may be traces of the liquid or semi-liquid vehicle remaining in the sample. In addition, there are the peaks resulting from actual pyrolysis of non-volatile ink constituents, and from the paper itself. Since less ink is applied than in the case for photocopy toner, the peaks from the paper generally make up a larger part of the chromatogram for ink analysis than for toner analysis.

Figure 10 shows the pyrogram resulting from pyrolyzing a 2mm^2 piece of paper with ball-point ink writing on it. All of the peaks labeled with numbers are cellulose pyrolysates from the paper. Peaks X and Y are from the ink vehicle and will show up in an independent headspace sampling at 2000, and consequently, they leave the sample before pyrolysis takes place. The peaks labeled A, B and C are pyrolysis products from the remaining, non-volatile residue of the ink. Just as with the cotton/polyester blend thread, and the photocopy toner on paper, the presence of several components in the sample causes little effect in the pyrolytic behavior of each individual material, and peaks A, B and C are seen if the ink is pyrolyzed alone or while it is on the paper.

Art Materials

Valuable art objects, including paintings, furniture and archeological artifacts are frequently investigated via pyrolysis of the non-volatile materials used in their construction. Paints, varnishes, glues, pigments, waxes and organic binder formulations have been studied from the aspects of both conservancy and authentication. The materials used for varnishes and other protective coatings, glues used in assembling pieces and other polymeric species change from region to region, time to time and even with specific artists and craftsmen, so that identification of these materials goes far to indicate the authenticity, and even age of a particular object. Natural resins used to formulate varnishes for centuries have been analyzed by Shedrinsky *et al.* (1988), showing good distinctions among dammar, mastic, sandarac and copals. Wright and Wheals (1987) have published results on natural gums, waxes and resins as they apply to Egyptian artifacts. Frequently art and archeological samples must be investigated in layers, since protective coatings are generally applied over the original artwork, which itself may have been applied onto a prepared surface. The identification may involve analysis of the binder user in a subsurface, the oil or resin in the artwork and the natural or synthetic polymer present in the protective coating.

An example of this is shown in Figure 11. The sample came from an Egyptian sarcophagus which was believed to originate from about the 4th century AD. The object was constructed of wood, which was covered with a white layer (the ground) of essentially inorganic material, used as a base for decorative paintings. It was decided to investigate the organic binder used in preparing the ground as a measure of the authenticity of the sarcophagus. If an ancient material had been used, the authenticity would be supported, if a modern adhesive was detected, the sarcophagus would be fraudulent. Various natural binder materials were proposed and investigated, including egg, wax, animal glue and copal resin. When a sample of the ground layer was pyrolyzed at 500ºC, the pyrogram matched that produced from ancient animal glue which had been independently authenticated.

An extensive review of pyrolysis applications in the analysis of artworks and antiquities has been published by Shedrinsky *et al.* (1989), with examples including glues and other adhesives, oil paints, varnishes, natural resins and reference to the famous Van Meegeren case.

CONCLUSION

Polymeric materials, whether natural such as cellulose, resins and proteins, or synthetic such as polyolefins, nylons and acrylics, behave in reproducible ways when exposed to pyrolysis temperatures. This permits the use of pyrolysis as a sample preparation technique to allow the analysis of complex materials using routine laboratory instruments. Pyrolytic devices may now be interfaced easily to gas chromatographs, mass spectrometers and FT-IR spectrometers, extending their use to solid,

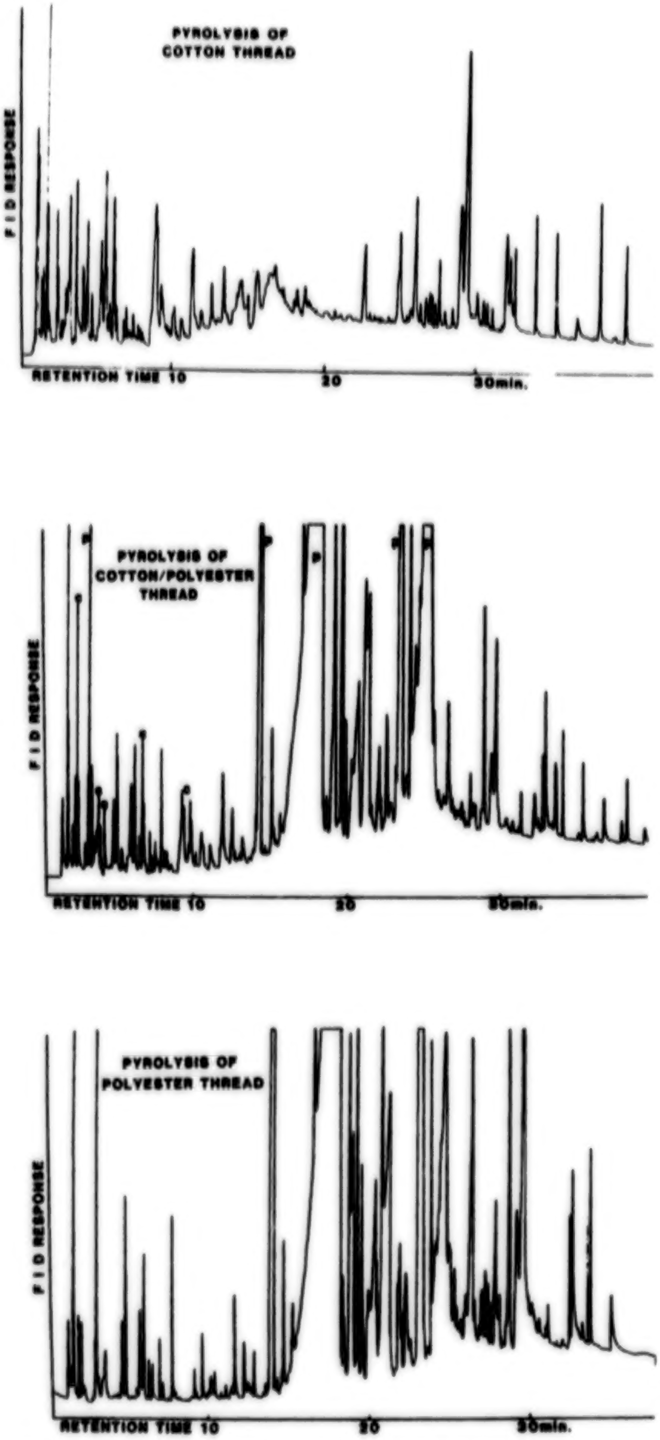


Figure 8. Comparison of pyrograms obtained from cotton (top), polyester (bottom) and cotton/polyester blend (center).

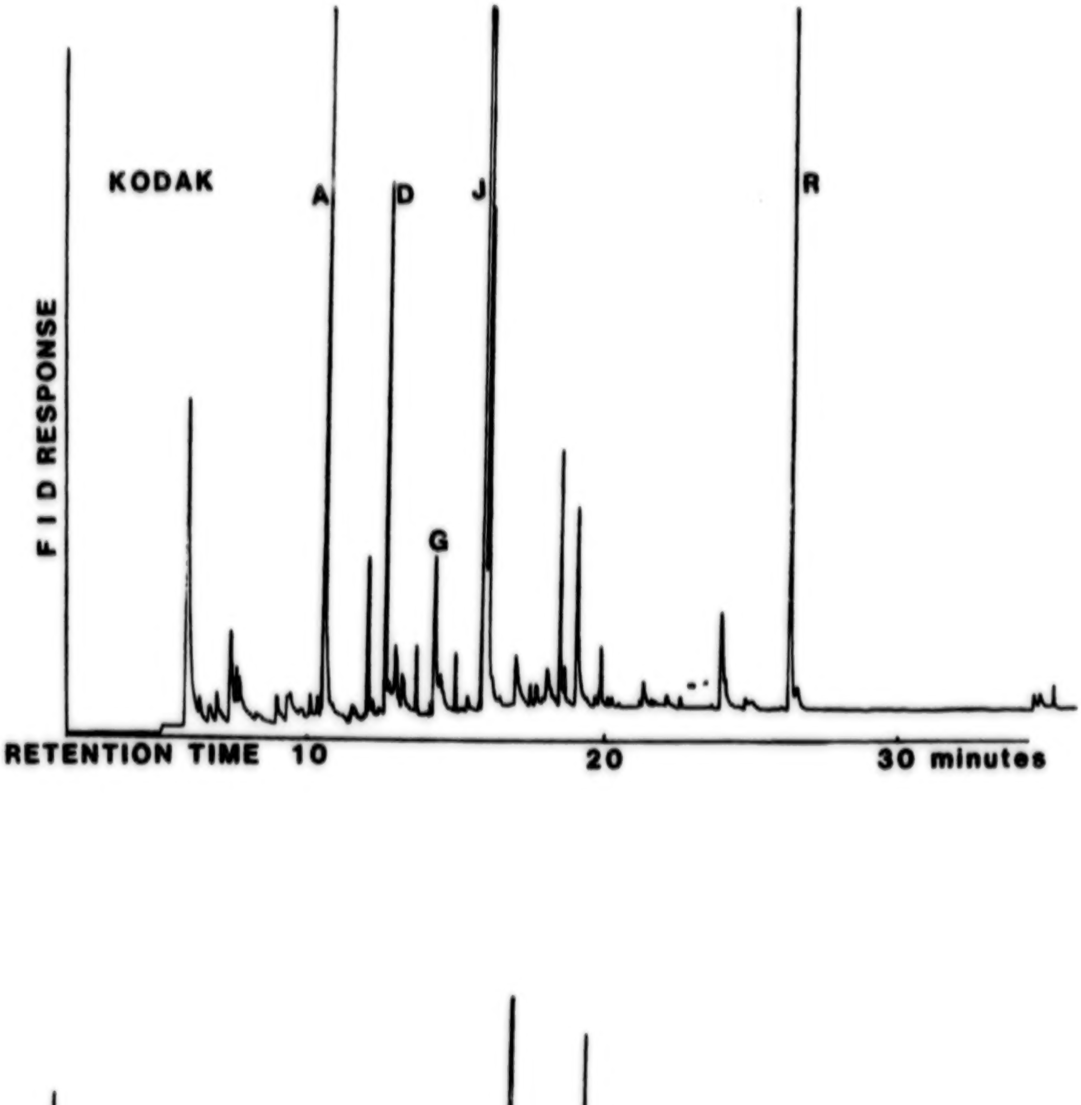


Figure 9. Comparison of Kodak and Xerox photocopy toners on paper.

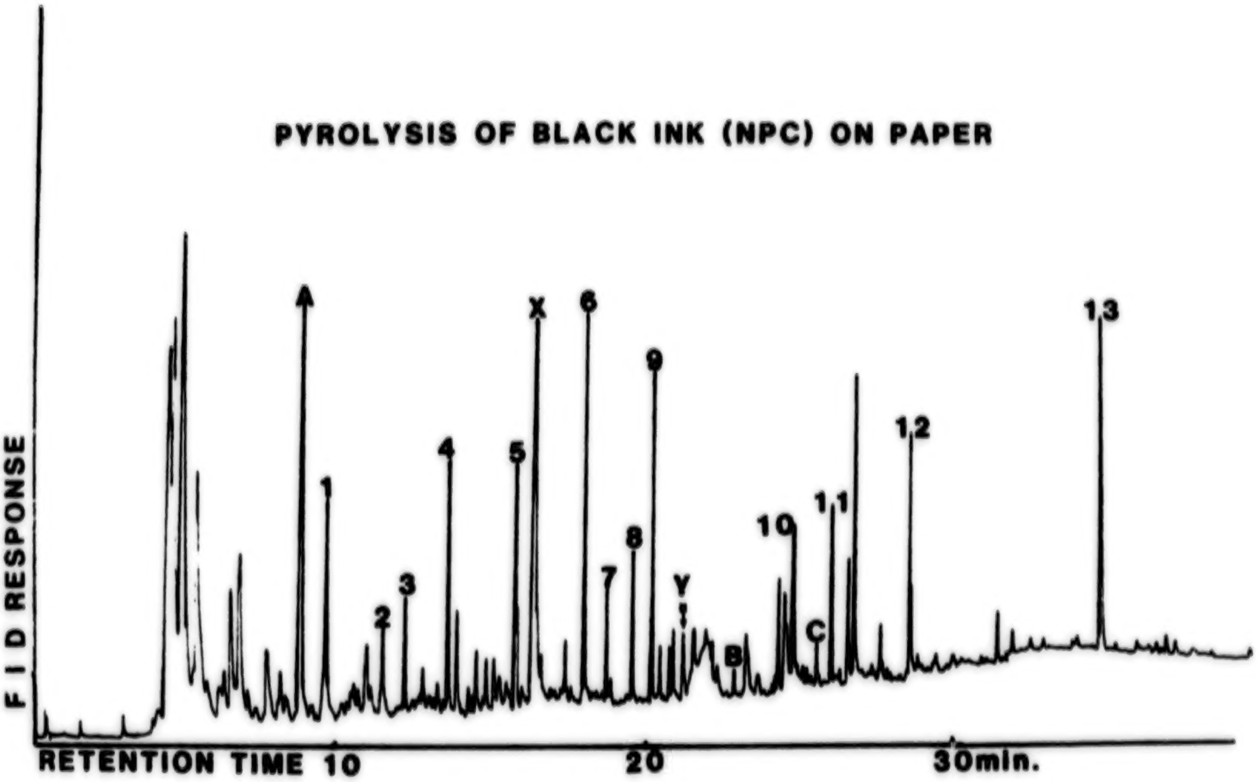


Figure 10. Pyrolysis of ball-point pen ink on paper. Numbered peaks result from paper pyrolysis, peaks A, B and C from pyrolysis of ink non-volatiles.

opaque and multi-component materials. Forensic laboratories have long made use of pyrolysis for the analysis of paint flakes, textile fibers, natural and synthetic rubber and adhesives. The list of applications has been expanded to include documents, artworks, biological materials, antiquities and other complex systems which may be analyzed with or without the separation of various layers and components involved.

REFERENCES

Fukuda, K. (1985). The pyrolysis gas chromatographic examination of Japanese car paint flakes, Foren. Sci. Internat. 29:227-236.

Hughes, C., Wheals, B. B. and Whitehouse, M. J. (1978). Pyrolysis-mass spectrometry of textile fibers, Analyst 103:482-491.

Irwin, W. I. (1982). Analytical Pyrolysis A Comprehensive Guide, Marcel Dekker, NY.

Lattimer, R. P. and Kroenke, W. J. (1980). The formation of volatile pyrolyzates from poly(vinyl chloride), J. Appl. Polymer Sci. 25:101-110.

Liebman, S. A. and Levy, E. J. (1985). Pyrolysis and GC in Polymer Analysis, Marcel Dekker, NY.

Morgan, S. L., Fox, A., Larsson, L. and Odham, G. (1990). Analytical Microbiology Methods, Chromatography and Mass Spectrometry, Plenum Press, NY.

Munson, T. O., McMinn, D. G. and Carlson, T. L. (1985). Pyrolysis-capillary gas chromatography-mass spectrometry for analysis of automotive paints, J. Foren. Sci. 30:1064-1073.

Saferstein, R. and Manura, J. J. (1977). Pyrolysis mass spectrometry - a new forensic science technique, J. Foren. Sci. 22:749-756.

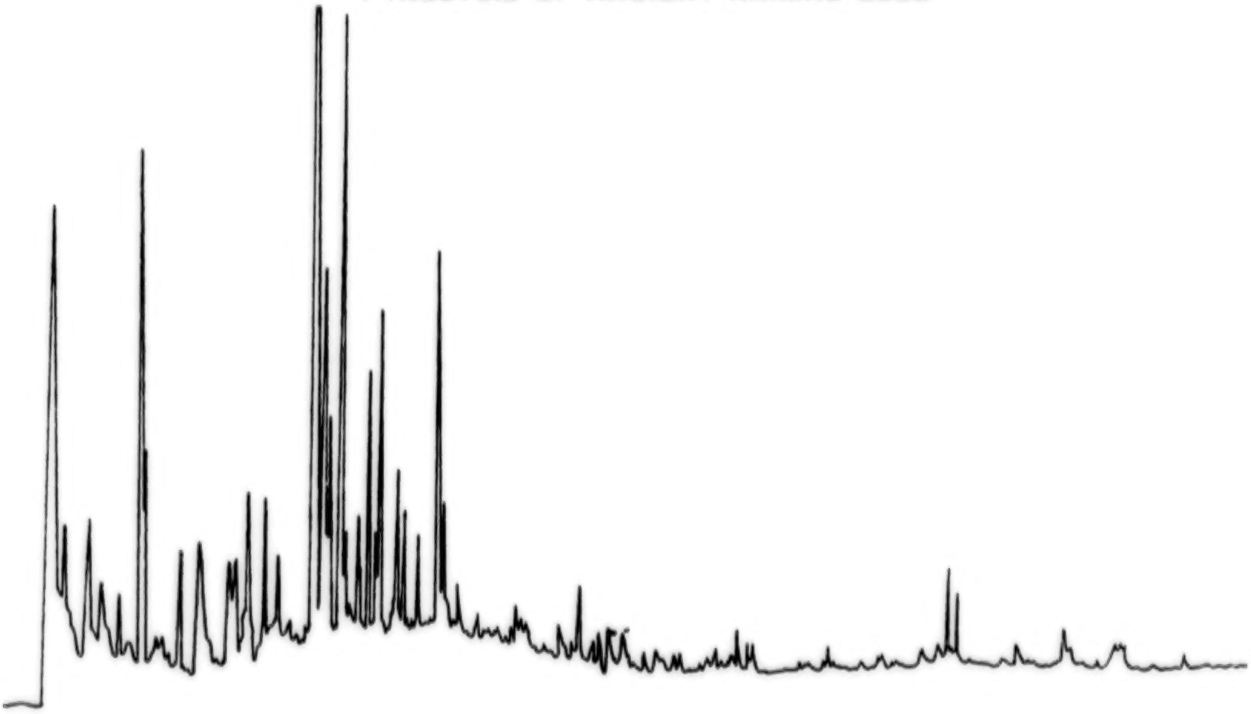
Saglam, M. (1986). Qualitative and quantitative analysis of methyl acrylate or methyl methacrylate of acrylonitrile fibers by pyrolysis gas chromatography, J. Appl. Polymer Sci. 32:5717-5726.

Shedrinsky, A. M., Wampler, T. P. and Baer, N. S. (1988). The identification of dammar, mastic, sandarac and copals by pyrolysis gas chromatography. In: Wiener Berichte uber Naturwissenschaft in der Kunst, VWGO pub., Wien.

Shedrinsky, A. M., Wampler, T. P., Indictor, N. and Baer, N. S. (1989). Application of analytical pyrolysis to problems in art and archeology: a review, J. Anal. Appl. Pyrolysis 15:393-412.

Tsuge, S., Sugimura, Y., Nagaya, T., Murata, T. and Takeda, T (1980). Microstructural characterization of polypropylenes by high-resolution pyrolysis-hydrogenation glass capillary gas chromatography, Macromolecules 13:928-932.

Tsuge, S., Ohtani, H., Nagaya, T. and Sugimura, Y. (1982). Studies on thermal degradation of aliphatic


PYROLYSIS OF ANCIENT ANIMAL GLUE

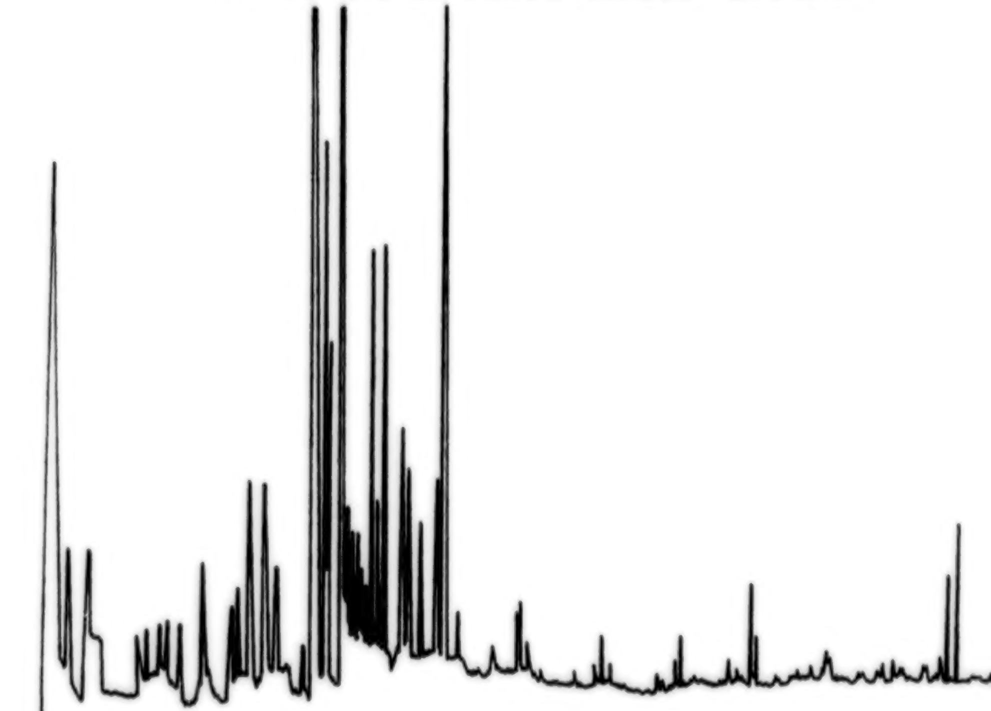

PYROLYSIS OF SARCOPHAGUS "GROUND"

Figure 11. Pyrolysis of Egyptian sarcophagus ground material for binder content, compared to sample of ancient animal glue.

polyamides by pyrolysis-glass capillary gas chromatography, J. Anal. Appl. Pyrolysis 4:117-131.

Wampler, T. P. (1989a). A selected bibliography of analytical pyrolysis applications 1980-1989, J. Anal. Appl. Pyrolysis 16:291-322.

Wampler, T. P. (1989b). Thermometric behavior of polyolefins, J. Anal. Appl. Pyrolysis 15:187-195.

Wampler, T. P. and Levy, E. J. (1987). Pyrolysis GC in the analysis of inks and papers, LC & GC 4(11):1112-1116.

Washall, J. W. and Wampler, T. P. (1989). Analytical pyrolysis of complex multicomponent samples, J. Chrom. Sci. 27:144-148.

Washall, J. W. and Wampler, T. P. (1991). Direct-pyrolysis Fourier Transform-infrared spectroscopy for polymer analysis, Spectroscopy 6(4):38-42.

Wheals, B. B. (1981). Analytical pyrolysis techniques in forensic science, J. Anal. Appl. Pyrolysis. 2:277-292.

Wright, M. M. and Wheals, B. B. (1987). Pyrolysis-mass spectrometry of natural gums, resins and waxes and its use for detecting such materials in ancient Egyptian mummy cases, J. Anal. Appl. Pyrolysis 11:195-212.

Zimmerman, J., Mooney, D. and Kimmet, M. J. (1986). Preliminary examination of machine copier toners by infrared spectrometry and pyrolysis gas chromatography, JFSCA 31(2):489-493.

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CRIMINALISTICS: THE FUTURE OF EXPERTISE

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Being an expert in any area of forensic science demands a range of qualities, some innate, some acquired through education, training and expertise. I am going to talk about three aspects of expertise which I will call: pattern identification; probabilistic judgement; and reasoning. I do not claim that these three are discretely distinct from each other, nor are they divorced from other aspects of expertise. However, they provide useful headings for talking about ways in which our discipline may evolve in years to come. They are areas which interest me particularly because of the time I have spent working on the application of statistical methods to forensic science problems.

Throughout the world, forensic scientists face growing challenges: the implementation of new and increasingly powerful techniques; increased demand from growing crime levels; balanced by increased pressure of budgetary restraint. In such environments it is tempting to concentrate on the purely technical and organizational aspects of our work. Techniques can be refined, organizations can be made slicker and more efficient. But the quality of the product which we deliver is determined by how good we are at handling observations and turning them into high quality information. This, I believe, is where the science of our craft lies. We are supposed to be the experts - can we also claim to be scientific in the application of our expertise?

PATTERN IDENTIFICATION

Here I consider that class of cases in which an expert compares two items and forms a categoric opinion that they have the same origin. A Canadian lawyer once described this to me as a state of "moral certainty". There are many different examples, of course, such as toolmarks, footwear marks, hand-writing, ballistics and fingerprints. I include the last because I am one of those who sees fingerprint examination as being essentially the same in fundamental nature as those other areas which we classify as forensic science or criminalistics. I also include it because it is an area which I have studied in some detail.

I started out my career as a handwriting expert; so I was carrying out the sort of careful detailed visual comparisons which can often lead to a categoric opinion. My view of forensic science was strongly influenced by a handful of papers which I read in those early days: in particular one by Paul L. Kirk entitled "The Ontogeny of Criminalistics" (1963). Professor Kirk was asking some searching questions about the nature of the pursuit of criminalistics - is it a science? Is it a profession? If it is a science then where are its fundamental principles? He said, for example:

> Many persons can identify the particular weapon that fired a bullet, but few if any can state a single fundamental principle of identification of firearms. Document examiners constantly identify handwriting, but a class of beginners studying under these some persons, would find it difficult indeed to distinguish the basic principles used.

Over the years a number of people have attempted to establish such principles through the application of statistical theory and methods. A paper by Stoney and Thornton (1986) is an impressive review, for example, of the attempts to place fingerprint individualization on a statistical basis. Because of my back- ground I was asked in 1989 by Dr. Ray Williams, former Director of the Metropolitan Police Forensic Science Laboratory, to work with him on a review of the British 16 point rule for fingerprint individualization. It was a fascinating study which brought me into contact with experts the world over.

Once you get inside this field, it does not take long to realize that identification rules based on a point count do not make a great deal of sense for any evidence type. After all, the decision as to whether a particular feature amounts to a significant similarity or a significant difference is highly subjective. Two experts looking at the same comparison might count widely different numbers of points of comparison. One of the experts who helped my thinking considerably was David Grieve of the Illinois State Police Bureau of Forensic Services and I quote from a paper which he sent me and which, I am glad to see, has since been published in Fingerprint Whorld (1990).

> There is a perverse side to human behavior that seems determined to have nature conform to man's concepts. All the efforts to "prove" the individuality of nature only reveal

> why man is the single species to visibly show the signs of embarrassment. The simple fact is that nature refuses to replicate biological exactness. The support this occurrence has from statistical study is irrelevant, for variation will continue regardless of man's proof of its existence or not. The issue, then, is not the establishment of individuality, but the ability to recognize sufficient information for the disclosure of that individuality. Man is stubbornly arrogant, and even though his mathematics are essentially meaningless to the whole, he attempts to apply it to the parts.

I do not pretend to understand the psychology of the process of individualization. It is a sophisticated function which is not confined to forensic activities. How is it that we can pick up an old school photograph for the first time and pick out from 500 faces the blurred and grainy image of a friend as he/she appeared maybe 20 years ago? How do we explain the mechanism by which an identification expert arrives at a conclusion in a state of moral certainty? In this latter connection I have had good cause to ponder over the last couple of years because of the work I have been doing on DNA statistics. With what statistical level can one equate the achievement of moral certainty: one in a million?; one in a billion? There is no answer to this question and I agree with David Stoney's remark at the 1990 International Association of Forensic Science Meeting - "you can not achieve individualization through statistics".

For similar reasons it is difficult to see the day when computers will be capable of doing what the identification expert does. It is impressive to see the capabilities of the modern computer fingerprint retrieval systems; systems which are the result of tens of millions of dollars of investment. Given a mark to search, the speed with which a large database is scanned is impressive. Yet what I find equally impressive is to see the dexterity with which a human expert takes the retrieved list of images and flicks through them: none being worth a second glance, save on the fortunate occasion when the right individual is in the system. This procedure represents to me a synergistic fusion of brain and computer which should guide our thoughts about the future of our science.

The computer is an immensely powerful tool for carrying out complex calculations and for rapidly searching large databases. But the human eye/brain has the power to identify patterns with 100% reliability. Our way forward is in the design and operation of systems which recognize these strengths and which exploits them to maximum effect. The technology known as Intelligent Knowledge Based Systems - often called expert systems - offers the tools for advancement.

However, while I recognize the identification power of the human eye/brain I believe that it should never be taken at face value. As will become clearer later, an expert becomes such in my eyes, not when be can claim to have done thousands of cases over tens of years, but when he has shown in repeated tests under controlled conditions that his judgement is up to the standards that a criminal justice systems expects. The growth of accreditation schemes, such as that run by the International Association of Identification for fingerprint experts, and of proficiency tests such as those run by Collaboration Testing Services are an essential bulwark to our scientific foundation.

PROBABILISTIC JUDGEMENT

In the majority of forensic cases the scientist will be giving not categoric but corroborative evidence. Sometimes the position will be relatively straightforward. For example, the evidence might consist of a bloodstain left at a crime scene which is the same type as that of a suspect. The evidential value in that instance is merely a function of the relative frequency of that blood type within a specified population (though just what the function is; and how the population is to be specified are issues which we could debate at length!). Scientists, lawyers and courts all agree on the importance of statistics in such situations. But what happens when things get more complicated? Let us turn to glass evidence.

Assume that a window has been smashed during a robbery. The clothing from a suspect is searched and two or three small glass fragments are found on its surface which are indistinguishable from the glass of the window at the crime scene. Statistics of refractive index distributions are of interest here but what is the most relevant distribution? Glass in windows, or glass found on clothing? Few would disagree that the latter is the relevant one. Unfortunately, however, such data are not readily available. Consider another aspect of the evidence: is this the quantity of glass we would have expected to find if the suspect has been at the scene? This is far from being a trivial question - depending as it does on the alleged circumstances of the crime and on how soon after the event the suspect was arrested. But surely it is a question that must be addressed.

There are two main questions which are relevant to assessing the evidential value in this case:

> What is the probability of the glass evidence if the suspect was at the crime scene?
>
> What is the probability of the glass evidence if the suspect was not at the crime scene?

To answer such questions we may be guided by disconnected snippets from the literature, or by the small scale surveys which have been done in various forensic science laboratories. But at the end of it all the answers are going to depend heavily on expert judgement.

In general, of course, forensic scientists are not accustomed to formalizing their interpretations through questions such as the above. Still less are they accustomed to providing numerical responses. Richard Pinchin (1993) demonstrated a computer advisory system for glass evidence called CAGE: a system which was developed by Pinchin and John Buckleton of the Department of Scientific and Industrial Research, New Zealand. The dialogue embodied in CAGE prompts the scientist to address questions of the above kind. It is quite amusing to see that the first reaction of the typical scientist is "I can not answer that!". Our response is - "if you can not answer the question, how can you interpret the evidence?" The reason is, of course, that we have traditionally muddled through - there has been no great demand to sharpen up our thinking.

I think we can agree that the questions about the probability of the glass evidence given various scenarios are highly relevant to interpretation. If we do not sharpen up our approach then, I believe, we can be accused of being unscientific. I would like to give you two reasons why I say this: psychological and epistemological.

The psychological aspect has been highlighted for me by some research which as been carried out by a colleague and friend of mine, Colin Brown (personal communication). Brown has taken a particular interest in psychological studies such as those reported in the book "Judgement Under Uncertainty: Heuristics and Biases" edited by Kahneman, Slovic and Tversky (Kahneman *et al.* 1982) - referred to as KST for short. It is abundantly clear from all of the research that has been carried out that people reason quite irrationally in the face of uncertainty. In particular a person's assessment of the likelihood of an event can be influenced by many different psychological factors. I will give two examples, but there are many more.

KST refer to "biases due to the retrievability of instances" and describe an experiment in which groups of volunteers were read lists of well-known personalities of both sexes and each group was asked subsequently to judge whether the list it had heard contained more names of men than of women. In some of the lists the men were relatively more famous than the women and in others the women more famous than the men. In each of the lists the subjects erroneously judged that the sex which had the more famous personalities was the more numerous. In relation to this example, KST say:

> In addition to familiarity, there are other factors, such as salience, which affect the retrievability of instances. For example, the impact of seeing a house burning on the subjective probability of such accidents is probably greater than the impact of reading about a fire in the local paper. Furthermore, recent occurrences are likely to be relatively more available than earlier occurrences. It is common experience that the subjective probability of traffic accidents rises temporarily when one sees a car overturned by the side of the road.

Next, I quote an example of what KST call "biases due to the effectiveness of a search set". I am going to sample a word (of three or more letters) at random from an English text. Which is more probable: that the first letter will be an "r", or that the third letter will be an "r"? It is much easier to recall words that have r in the first position and so most people judge the first alternative to be the more probable: it isn't - words with r as the third letter are more common.

Colin Brown (personal communication) has carried out a range of similar experiments on forensic scientists and has found that they are no better at reasoning in the face of uncertainty then groups such as those studied by KST. This is hardly surprising: scientists are not, in general, trained to carry out such tasks. Our scientists are expected to acquire the means of evaluating uncertain situations by some mysterious process of omosis leading to what we call "experience". Let us turn to the epistemological view.

Contributing to a debate on clinical trials in the British Medical Journal (1983), Michael Baum said:

> The trouble with "experience" as a way of approximating to reliable knowledge is that all of us tend to reinterpret each individual experience in the light of a previously held conceptual framework.

Note the phrase "reliable knowledge". Our substitute for it in forensic science is often the experience that we gain from examination of a long succession of events which are hardly representative of the world at large. If I say "this is not what I would expect to see on the clothing of a man selected at random from the population?" I have to ask myself just how much reliable knowledge I have of the clothing of men selected at random. If I say "this is the quantity of glass I would expect to see if the suspect is the man who smashed the scene window?" I have to ask just how much reliable knowledge I have of windows being smashed under controlled conditions.

A quotation from Karl Popper (1972) has always struck me as highly relevant to our field. I am taking him slightly out of context because he was talking about the way in which the classical psychoanalysts continually modified and elaborated their hypotheses to fit new evidence, but the tale is a cautionary one for forensic scientists also:

> Once, in 1919, I reported to him (Adler) a case which to me did not seem particularly

> Adlerian, but which he found no difficulty in analyzing in terms of his theory of inferiority feelings, although he had not even seen the child. Slightly shocked, I asked him how he could be so sure. 'Because of my thousand fold experience', he replied: whereupon I could not help saying: 'And with this new case, I suppose, your experience has become one thousand-and-one-fold'.

As forensic scientists we face frequent temptation to fall into similar traps. Frankly, I do not believe that our claims of experience count for much unless we can show that our knowledge is subject to repeated testing under controlled conditions. Statisticians call this process "calibration". Let me explain how the glass advisory system CAGE (Pinchin 1993) provides a framework for establishing structured, reliable and corporate knowledge.

One of the questions which is posed to the user during the computer dialogue is: "given the circumstances of this incident, if the suspect is the person who smashed the scene window what is the probability that some glass would be found on his clothing?" Before posing the question, the computer program gives the user the opportunity to review:

(a) The rather scant literature on the subject, and
(b) A "knowledge base" which consists of a record of what other scientists have responded to the same question in similar circumstances on previous occasions.

The scientist then gives his response and moves on to the next question. At the end of that case session the scientist is given the opportunity of adding his probability to the knowledge base. In this way the pool of advice for the future users grows.

When we started this project, I have already explained that scientists found it extraordinarily difficult to give probabilities and so John Buckleton and I created an embryo knowledge base incorporating our own assessment in a range of circumstances. What right or authority did we have to do so? Practically none - but it was amazing to see how it stimulated people into thinking. It is fairly easy to see why. It is because, in general, it is easier to say what you do not like to what you do like. So, in another situation we might have a dialogue like:

> "What is the probability of rain spoiling the picnic?"
> "I do not know".
> "Could it be a 90% probability?"
> "Oh no - it is nothing like as high as that".

So our embryo base served the purpose of focussing the user's thinking. They, in turn, added their assessments to the base so increasing its scope and ownership.

But of course, you may well have already seen the potential flaw in all of this: we may be building, not a knowledge base, but an ignorance base! For all we know, our collective wisdom is not a good reflection of reality. This is where the next, crucially important, phase of our paradigm arises.

After we have allowed the knowledge base to grow for a period we can carry out a critical review. More specially, we can design experiments to model the most common situations in our knowledge base. When we carry out the experiments we have an excellent check of how our experts' thought patterns approximate to reality. This is the procedure known as "calibration" it is one of the most exciting prospects of this approach.

In the past there have been many good attempts by scientists to collect data from realistic situations. Almost invariably these are expensive exercises and the payback in terms of increased information in the scientist's statement is generally difficult to detect. Those who have conducted glass smashing experiments will know how much time and effort are necessary to gain information of scientific value from the smashing of even a few windows - apart from the physical risks involved! Now, through knowledge based systems we can target future collection activities to those areas where scientists demonstrate greatest uncertainty: these are easily determined from the knowledge base. Because we will have a clearer idea of the information we most need we will be better placed to use the results of our research more effectively than in the past. The days of "well, here is the data, what shall I do with it?" should pass. There should be a continuing cycle of - knowledge elicitation - calibration - new data - knowledge refinement. This is not a bizarre pipe dream. Intelligent knowledge based systems are being developed and used in many areas - medical diagnosis, for example - which have similar requirements of experts and expertise as our own field.

REASONING

I have talked about assessing one uncertain event at a time. In a casework examination there are, of course, many different observations, all with associated uncertainties. These might include hard statistics - such as "18,000 sweaters of this type have been sold" or "5% of vehicle glass has this composition" - and "soft" probabilities of the kind in the previous section. How should they all hang together? At present we rely on intuition and what may be described as the "conservatism heuristic"; this is the unwritten rule that, provided we err on the side of the defendant, then everything will be alright. This can be sloppy and unscientific. What is more, it is not always obvious what the conservative approach is in a particular case. A simple example will illustrate this point.

The evidence consists of a bloodstain at the crime scene which matches the type of the defendant. The frequency of that type is 1 in 100 and we can all agree that that statistic is relevant in some way to the assessment of the evidence. Now consider a second case in which two men committed the crime, there are two bloodstains of different types with relative frequencies of 1 in 100 and 1 in 1000. There is a single defendant who matches the 1 in 100 stain. The conventional approach in this situation is to ask "if I take a person at random, what is the chance he would match one or other of the stains?" The answer to this question is 0.01 + 0.001 = 0.011. We might convince ourselves that we are being fair to the defendant by considering a wider range of possibilities than in the first case. However, it is quite easy to show (Evett 1987) that this is not right. The right answer, in frequency terms, amounts to doubling the 1 in 100 frequency, that is, 0.02. "Aha!", I hear you say; "whether you say 0.01, 0.011 or 0.02 will not make a scrap of difference to the impact which the evidence has on the jury". That is not the point. We are the scientists and if we have a choice between doing things the right way or the wrong way then we have no business to choose the latter just because we do not know any better.

Let me turn to an error which is far more common. I do not believe that it is the sort of error which leads to false convictions, but what concerns me is that it is fundamentally unscientific. It is known as the "fallacy of the transposed conditional", though Thompson and Schuman (1987) call it the "prosecutor's fallacy". Returning to our simple blood typing example, with one stain, it proceeds as follows.

The probability that the crime stain would be of that type if someone other than the suspect left it is 1 in 100. Therefore the probability that someone other than the suspect left the crime stain is 1 in 100. Or, putting this statement another way, and confusing odds with probabilities it may be argued that the odds are 100 to 1 against some other person having left the crime stain.

The argument is utter nonsense because the second sentence does not follow from the first. The third sentence merely compounds the error. The second sentence embodies the fallacy. It is exactly like saying: the probability of throwing a 4 with an unloaded die is 1/6; so if I do throw a 4 then the probability that the die is unloaded is 1/6; so if I throw a 4 there is a 5/6 probability that the die is loaded. Try explaining that to a craps player!

Thompson and Schuman (1987) addressed their observations primarily to the legal community. The prosecutor's fallacy is ubiquitous among legal practitioners. But we can forgive a lawyer such logical weaknesses because, after all, he has not had the benefit of a scientific training. Surely a forensic scientist can not be excused in the same way?

I repeat that I do not believe that the fallacy leads to incorrect convictions but if we are to advance as scientists within a scientific discipline then we ought to agree on some basic issues such as the class of questions which we can address and those which we can't address. In general, it is just not possible on scientific evidence alone to answer a question of the type "what is the probability that this man left that blood stain?". But it is, in general, possible to answer questions of the type "what is the probability of the evidence if the man left the blood stain?" and "what is the probability of the evidence if someone else left the blood stain?" It is the ratio of the answers to these two questions which determines the strength of the evidence.

CONCLUSION

So, to return to my title - what is the future of expertise in criminalistics? I propose four examples which encapsulate the ethos of unscientific expertise:

Mystique

"When you have been doing the job
as long as I have ..."

Intuition

"I rely on my gut feeling ..."

Complacency

"I have done thousands of cases and I
have never been shown to be wrong..."

Entrenchment

"It has stood the test of time ..."

On the other hand, I propose four which encapsulate the ethos of scientific expertise:

Study and Debate

"What are our fundamental principles?"

Continuous Improvement

"Why do I do it this way? Is there a
better way?"

Self-analysis

"Why do I think this?"

Calibration

"Am I as good as I think I am?"

Our science still has a long way to develop. Indeed, many of the questions posed by Professor Kirk in 1963 remain unanswered. It is still true to say, as he did then, that:

> With all the progress that has been made ... careful examination shows that for the most part, progress has been technical rather than fundamental, practical rather than theoretical, transient rather than permanent ....In short, there exists in the field of criminalistics a serious deficiency in basic theory and principles, as contrasted with the large assortment of effective technical procedures.

If I could use one phrase to sum up the theme for the future development it is "knowledge management". We know how to manage finance; to manage staff; to manage techniques and procedures: what about one of our most precious resources - knowledge? We need systems to pool our knowledge; to structure our knowledge; to test our knowledge; to bring the best knowledge to bear on each aspect of every case. These are exciting prospects: this is the future of expertise in criminalistics.

REFERENCES

Baum, M. (1983). The controlled trial and the advance of reliable knowledge, Brit. Med. J. 287:1216-1217.

Evett, I. W. (1987). On meaningful questions: a two trace transfer problem, J. Foren. Sci. Soc. 27:376-381.

Grieve, D. (1990). Reflections on quality standards - an American viewpoint, Fingerprint Whorld 15:108-111.

Kahneman, D., Slovic, P. and Tversky, A. (1982). Judgement Under Uncertainty: Heuristics and Biases, Cambridge University Press, Cambridge UK

Kirk, P. L. (1963). The ontogeny of criminalistics, J. Crim. Law. Criminol. Police Sci. 54:235-238.

Pinchin, R. (1993). A Use of Expert Systems in Forensic Science, In: The Proceedings of an International Symposium on the Forensic Aspects of Trace Evidence, U. S. Government Printing Office, Washington, D. C., pp.

Popper, K. (1972). Conjectures and Refutations. The Growth of Scientific Knowledge, Routledge and Kegan Paul Ltd, London.

Stoney, D. A. and Thornton, J. I. (1986). A critical analysis of quantitative fingerprint individuality models, J. Foren. Sci. 31:1187-1216.

Thompson, W. C. and Schuman, E. L. (1987). Interpretation of statistical evidence in criminal trials. The prosecutor's fallacy and the defence attorney's fallacy, Law and Human Behavior 11:167-187.

SECTION II

EXTENDED ABSTRACTS

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THE CHEMISTRY AND INDUSTRIAL APPLICATION OF ACRYLIC BASECOAT/CLEARCOAT AUTOMOTIVE TOPCOATS

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During the late 1970's and early 1980's a new type of automotive topcoat system was being developed - the basecoat/clearcoat system. This system consists of a colored basecoat and an unpigmented clearcoat which imparts protection and a glossy finish. This system is an improvement over the lacquers in that the basecoat/clearcoat system is a thermoset or convertible system. Unlike the lacquers, which harden by solvent evaporation and can become liquid by the addition of a solvent, the basecoat/clearcoat system is crosslinked and therefore no amount of solvent will put it back into solution.

As just mentioned, the basecoat/clearcoat finish is a thermoset system which crosslinks upon baking. The vehicle or resinous portion of the basecoat and the clearcoat is made up of an acrylic resin and a melamine resin. The acrylic resin imparts various properties desired in the coating, namely durability, flexibility, stain and weather resistance. The acrylic resin is mixed with the melamine resin which is the crosslinking agent. Depending upon the functional groups in the acrylic resin, three types of linkages can form: an ether linkage, or an amide linkage. A third type of resin may be added to the vehicle of the system. This is an acrylic polymer in emulsion form and is usually a proprietary resin for the coatings manufacturer.

The acrylic polymer/melamine crosslinking resin system is used as the vehicle for both the basecoat and clearcoat. There are other materials in these topcoats which impart color and protection from ultraviolet (UV) radiation: pigments and additives.

There are four types of pigments: organic, inorganic, metal flake, and pearlescent. The organic pigments (bright, vivid colors and the inorganic pigments (opaque, dull earth-tones) are powders that are dispersed in a resin, then this is blended into the paint. The metal flake pigments impart a glitter to the final finish; these are also opaque pigments. Aluminum metal is used for automotive finishes and is purchased in paste form. This paste is mixed with a solvent and added to the paint. The pearlescent pigments give the automotive topcoat a satiny finish and are usually used along with the aluminum flake. This pigment is made of mica flakes coated with either titanium dioxide (TiO_2) or red iron oxide (an inorganic pigment). This pigment is very delicate and must be gently mixed with resin before it is added to the paint.

To combat the degradation due to sunlight, UV absorbers and hindered amine light stabilizers (HALS) are added to the clearcoat. UV absorbers work by converting the energy from UV radiation into heat and the HALS dissipates the UV radiation by an energy transfer mechanism.

Once the paint is made it will be applied to the job piece by spray application. Air atomization is one method of spraying where the paint is broken up into small particles and is forced onto the job piece by air pressure. Electrostatic application gives a negative charge to the paint which is drawn to the grounded job piece. A hybrid of the two, air atomized electrostatic application, combines the advantages of both for an efficiently applied, good-looking finish.

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IDENTIFICATION OF PAINT PIGMENT SUBLIMATES BY OPTICAL CRYSTALLOGRAPHY

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Paint pigment sublimates provide purified samples of sufficiently large particle size for rapid characterization using optical crystallographic methods. We have sublimed pigment samples and paint chips using three methods: (1) on a microscope slide from the slide onto the underside of the coverslip, (2) from a spot plate onto the underside of a coverslip using a hot plate, and (3) within a capillary tube.

Pigments vary considerably in their ease and temperature of sublimation. The more costly pigments, including most automobile paints, are specifically developed to be heat resistant. For most paint applications less expensive pigments are used. About half of the pigments we tested gave sufficient sublimation for characterization. For complete optical crystallographic description large, more slowly grown crystals were obtained by the spot plate/hot plate method. Using a white porcelain spot plate a few mg of pigment were placed in a well. A round cover slip, smaller than the mouth of the well, was then placed over the sample. The spot plate was then heated on a hot plate and the formation of sublimate monitored with a steromicroscope. More rapid, but less controlled sublimation follows from heating a small sample on a microscope slide under a coverslip. This method was satisfactory for easily sublimed pigments. It was helpful to remount the coverslip in order to separate the sublimate from any remaining unsublimed pigment. For paint chips a capillary method, suggested by Palenik (personal communication), was most effective. One end of a capillary tube was sealed. The sample was introduced at the opposite end and moved to the bottom by gently tapping the capillary. The capillary tubes were heated on a hot plate or over a flame. Sublimates can be examined directly in the capillary tube or removed by scoring the tube and transferring with a tungsten needle.

We have fully characterized a number of yellow pigments in the chemical group known as Hansa Yellows. Crystal form, habit and optical properties rapidly distinguish most of these pigments from one another. This work demonstrates the potential of the method. Implementation for most forensic samples requires that sensitivity be determined for pigments bound in coating films and that a link with pyrolysis gas chromatography be established. For paint chips, sublimation within capillary tubes provides the required sensitivity.

Advantages of the method are its low cost, possible link with pyrolytic methods of paint analysis and suitability as a preparative method for microspectrophotometry. The method is complicated by crystal polymorphism that is, in part, dependent on the conditions of sublimation.

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MICRO-FTIR ANALYSIS OF PAINT

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An Oregon State Police officer was struck by a vehicle driven by a man whose son was being taken into custody on an arrest warrant. The officer stated he jumped up just before impact, and landed on the hood of the vehicle. The driver denied hitting the officer at all. When the suspect vehicle was located, a black smear was located on the hood. The vehicle paint with the smear was chipped off and submitted with the officer's gun belt for analysis.

EXPERIMENTAL PROCEDURE

The smear was very small so it was submitted to the trace evidence section for analysis. Inorganic analysis was performed on a Tra-cor X-ray Fluorescence Spectrometer. Organic analysis was performed on a Spectra-Tech IR Plan microscope optically bridged to a Nicolet 710 FTIR Spectrometer. Reflectance analysis was performed, but transmission data yielded more definitive results. The smear was removed with a tungsten probe and applied to a NaCl disc with a single KBr granule for background measurement. A companion NaCl disc was applied and both placed into a Spectra-Tech squisher cell. The FTIR transmission data was obtained on both the smear and the officer's gun belt paint. Both were then run against the Hummel Polymer Library.

RESULTS

The IR data between the gun belt paint and the smear show a match. They are both identified by library search as most probably an alkyd resin. Confirmation of this was not available due to the manufacturer's claim to propriety interest. Inorganic analysis showed no strong inorganic pigment. Since the product is black, carbon is suspected as the pigment.

SUMMARY

Analysis showed the paint to be where the officer said he was struck while disproving the suspect's statements. The suspect pled guilty.

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ANALYSIS AND IDENTIFICATION OF PHOTOCOPIED TONERS

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There has been an increase in criminal cases in Japan using photocopiers, for example in blackmail cases. Identification of the manufacturers of photocopiers is an investigative problem of great interest to forensic investigations. As an aid to identify the manufacturers of photocopiers, morphological and chemical analyses of toners are conducted. Identification and discrimination of toners have been carried out using various instrumental analytical methods, such as SEM/EDX, FT-IR, Pyr-GC/MS and HPLC. In addition to the analyses of toners, fluorescence of PPC paper used is also measured by microspectrophotometer.

The differences of surface morphology of dry toners observed by SEM are shown in Figure 1. Photocopy conditions, such as temperature and pressure together with species of toners are standardized, according to the machine. Significant differences were not observed among the same model of machines and toners. Elemental analysis makes it possible to identify the toner, such as a single or dual components toner. There is also much information on the specific external additives, which are useful to discriminate the toner supplier. Characteristic elements were Si, Ti, Al, Mn and Cr. For example, Cr was added to prevent a charge up of the toner particle. The resin in the toner was analyzed by FT-IR and Pyr-GC/MS, and in almost cases, styrene/acrylate (sometimes methacrylate) copolymer with styrene as a dominant component were used.

Small differences were observed among them on their IR spectra. Sometimes, on the IR spectra of toners, the absorption at 2090 cm^{-1} was observed, and in these toners, a small amount of Fe was also simultaneously detected. This material was considered to contain a Prussian blue, which is added as a black agent. Pyr-GC was also applied to the differentiation of resins. The combination of MS analysis enables us to identify the pyro-

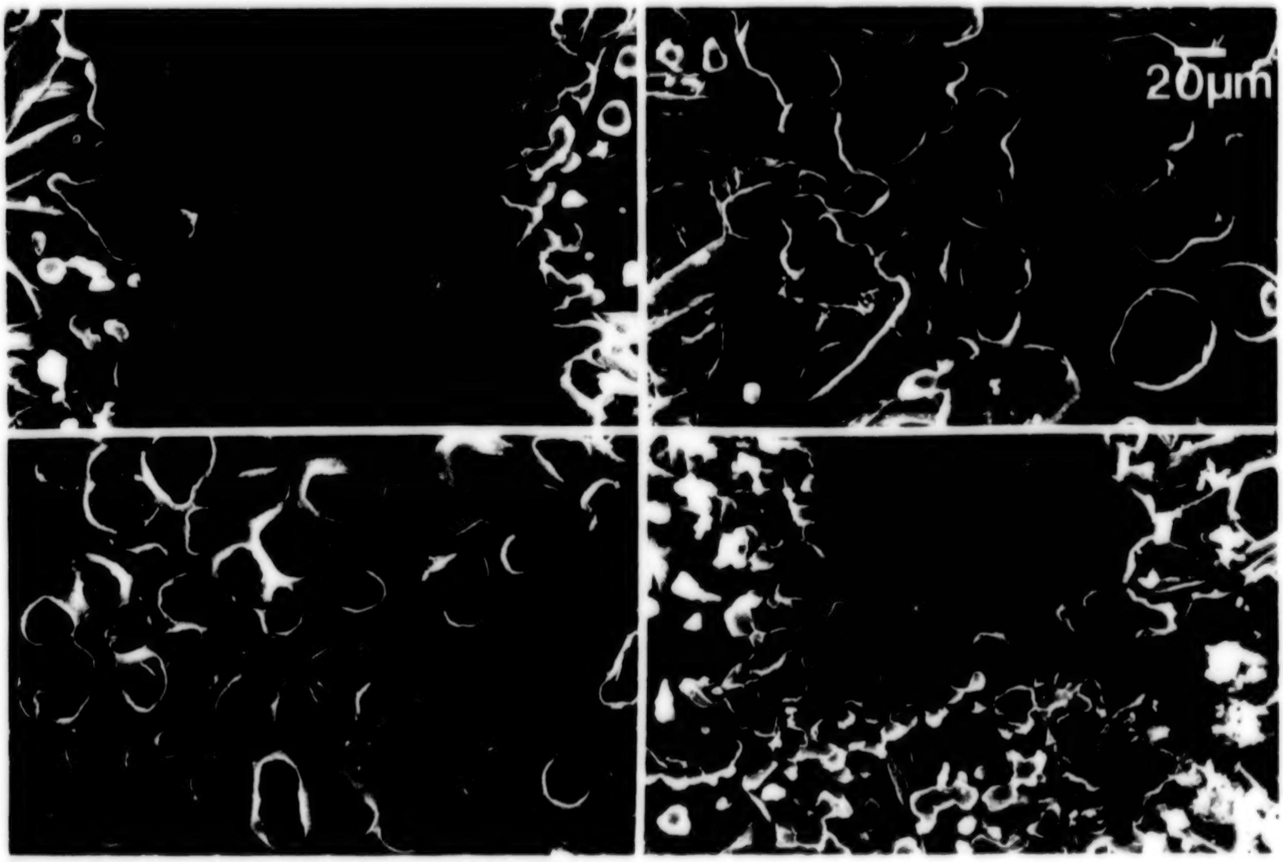

Figure 1. Surface morphology of dry toner as recorded by SEM.

lyzed products on their pyrogram. In this experiment, benzene, toluene, styrene, -methylstyrene, styrene dimer and styrene trimer were identified. It was possible to perform a discrimination of resins by the comparison of their ratio of these pyrolyzed products and other unknown peaks on their pyrogram. High performance liquid chromatography of toner extracts using reversed phase column and acetonitrile-H_2O (4:1) as a mobile phase gave characteristic chromatogram patterns. In addition to these toner analyses, fluorescence of PPC paper was measured by microspectrophotometer.

The combination of these analyses was applied to real kidnap and homicide cases. Figure 2 shows the ash obtained from a suspect's house (2a), and tip of burned photocopied paper was found in it (2b). Part (with a portion of a character/letter) of this ashed paper was analyzed by SEM/EDX, and dominant element was Fe, and also trace Mn was detected, but Cr was not observed. From these results, this part was considered to be photocopied character using a single component toner. The toner which had this element composition was specified to be only one machine supplier. The blackmail sent to the victim's house (2c) was identified to be photocopied by the same supplier's machine.

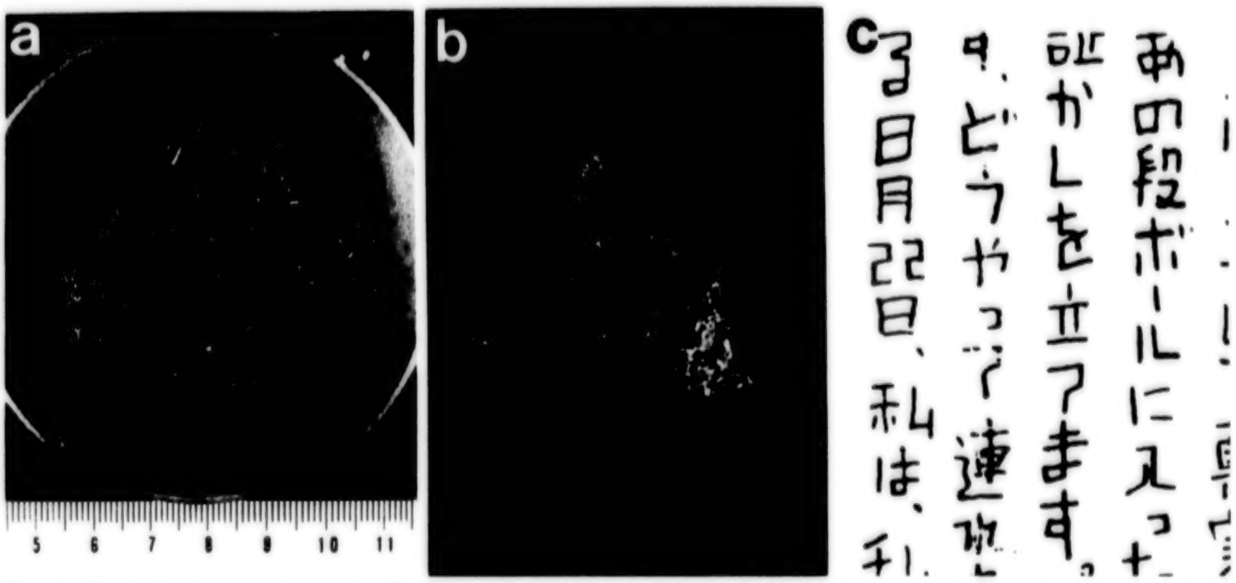

Figure 2. Real case of toner material identified by present procedure. (a) Seized ash obtained from suspect's home, (b) burned paper in the ash (with portion of character/letter), and (c) portion of blackmail letter sent to victim's house.

DISCRIMINATION OF AUTOMOBILE TIRE RUBBER

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Tire rubber is one of the most common traces submitted to forensic laboratories. Generally in the form of smears, the samples may originate from automobiles involved in hit-and-run accidents. In order to establish a common origin of questioned and control samples from a suspect's automobile, various instrumental analyses such as Fourier transform infrared spectrometer (FT-IR), pyrolysis gas chromatograph/mass spectrometer (Py-GC/MS) and energy dispersive X-ray microanalyzer combined with a scanning electron microscope (SEM-EDX) were used. In this study, 40 tire samples were analyzed.

After heat-sealing an end of a capillary glass tube (1 mm i.d.), a sample was placed into the tube near the sealed end. Thermal degradation was accomplished by heating, and the degradation product collected at the open end of the tube was placed on a KBr disk, followed by analysis by FT-IR (Analect AQS-20).

Py-GC/MS system used here consisted of a Curie point pyrolyzer (Japan Analytical Industry JHP-3S), a gas chromatograph (Varian 3500) and a mass spectrometer (Finnigan MAT ITD-800). A fused silica capillary column (30 x 0.25 mm i.d.) coated with methylsilicone (DB-1 J & W) was used with temperature programming from 50°C (1 min hold) to 100°C at a rate of 15°C/min and from 100°C to 280°C at a rate of 10°C/min. The carrier gas was helium and the flow rate was 1.0 ml/min with a splitting ratio of 1:50. The tire samples were pyrolyzed at 500°C for 5 sec.

A scanning electron microscope (Elionix EXM-3500) equipped with an energy dispersive X-ray analyzer (Ortec) was used for the samples ashed by electric furnace at the temperature of 600°C for 30 min.

Tire treads are made from isoprene rubber (natural rubber NR), butadiene rubber (BR) and styrene-butadiene rubber (SBR), or mixture of those with various additives. Rubber components, such as NR, SBR, NR/BR, NR/SBR, etc, were identified by FT-IR. As pyrolyzed products (vinylcyclohexene (VCH), styrene (ST), dipentene (DP)) were identified, more detailed discrimination of tire samples was conducted by evaluation of the peak area ratio of VCH/(VCH+ST+DP) and ST/(VCH+ST+DP). Inorganic elements were analyzed by SEM-EDX. The samples were classified by the contents of Calcium and Silicon.

Sample amount of 100 µg allows us to apply the whole methods described above, and at least 10 µg sample was required to conduct a single examination with Py-GC/MS, which gives the most detailed discrimination among those techniques studied here. On the basis of the results, 40 tire samples were classified into 27 groups.

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IDENTIFICATION AND COMPARISON OF POLYURETHANE FOAM PARTICLES BY FTNMR AND COMPARISON MICROSCOPY

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Los Angeles, California

Two double homicides, approximately 200 miles and one week apart were associated by foam particles distributed in the periphery of the victims' gunshot wounds. Shredded foam, packed into the shell of a homemade silencer was repeatedly propelled from the silencer by each successive muzzle blast. Type and caliber, as well as microscopic comparison, were precluded by the extensive damage to the bullets. The only evidence, of any kind, linking these murders, was the shredded foam particles strewn about the two crime scenes. These samples were compared microscopically and by Fourier Transform Nuclear Magnetic Resonance Spectroscopy (FTNMR) in order to associate these crimes with each other and eventually with their perpetrator(s).

INSTRUMENTAL ANALYSIS

The 50 Mhz Carbon-13 spectra were used to identify the particular plastic and to ascertain additional structural features about the polymer (Figures 1 and 2 depict these spectra for the two crime scenes). In addition, 200 Mhz Proton spectra were used to compare the molecular weights of the polymers as well as the batch formulation chemistry (Figures 3 and 4 depict these spectra for the two crime scenes). Each flexible foam sample (approximately 100 mg) was treated with 2 ml of DMSO-d_6 at 110°C in a sealed test tube for 2 hours. At the end of this time each sample had dissolved to yield a clear gray solution. The solutions were quantitatively transferred to labeled 5 mm high precision NMR tubes. All Carbon-13 spectra of the sample solutions were recorded at 50.3 Mhz on a Varian VXR-200 Fourier Transform Nuclear Magnetic Resonance (NMR) Spectrometer operating at 80°C. The Proton NMR spectra were recorded at 200 Mhz under the same conditions. Instrument parameters are shown in Tables 1 and 2.

MICROSCOPIC ANALYSIS

Microscopic examination of the flexible foam samples showed similarities in cellular structure (bubble size and networking) as well as color. Color may be the result of pigment deliberately added to the polymer or the result of aging. Since polyurethane yellows upon exposure to ultraviolet radiation, color can be indicative of relative sample age. This ultraviolet degradation is also manifested in the NMR spectra as the polymer degradation by-products.

The dismantled silencer, recovered one year later buried in a highway median, still contained microscopic particles, adhering to the interior surface. These particles could only be associated with the other foam samples by comparison microscopy due to the extremely small sample size.

CONCLUSION

FTNMR provides detailed and accurate information for the identification and comparison of polymers. Although seldom used in a forensic setting, FTNMR of soluble samples as small as 100 mg can yield clear, concise data about the structure of polymers and the formulation chemistry used in the manufacturing process. The finished molecular weight of a polymer and the side reaction by-products are manufacturing variables which will differ from batch to batch. These will be influenced not only by the basic ingredients, but also by temperature, humidity, and contaminants. In addition, catalysts, fillers, flame retardants, and monomer mixing proportions are subject to variance which is reflected in the spectra.

Table 1. PARAMETERS FOR RECORDING CARBON-13 NMR SPECTRA

frequency	50.309 MHz
spectral width	10000 Hz
acquisition time	1.638 sec
pulse width	90 degrees
temperature	80°C/353°K
number of repetitions	30000–40000
line broadening	1.0 Hz
FT size	32 K
total time	14–18 hours

Table 2. PARAMETERS FOR RECORDING PROTON NMR SPECTRA

frequency	200.058 MHz
spectral width	4000 Hz
acquisition time	3.752 sec
pulse width	54 degrees
temperature	80°C/353°K
number of repetitions	48
line broadening	none
FT size	32 K
total time	3 minutes

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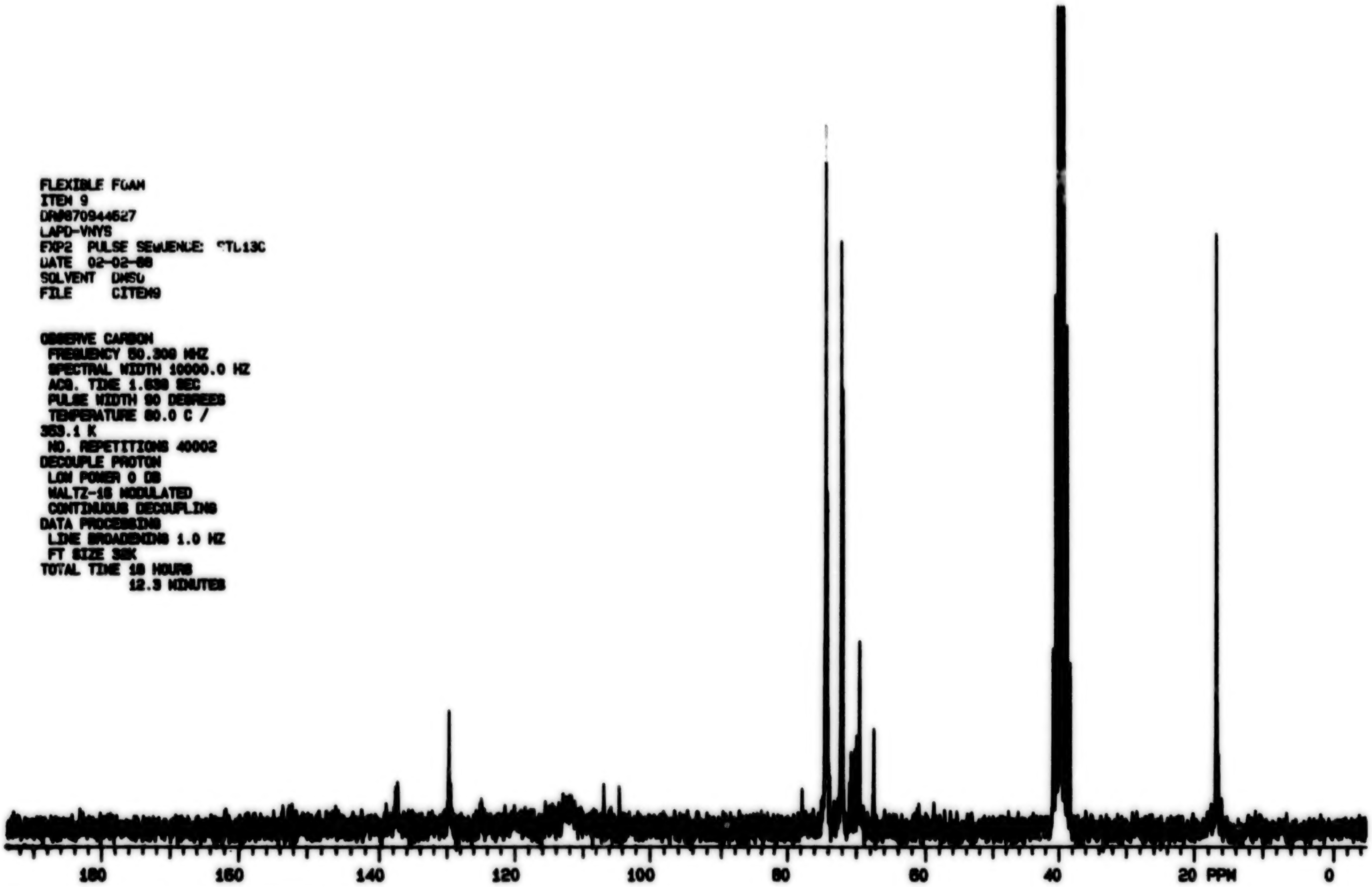
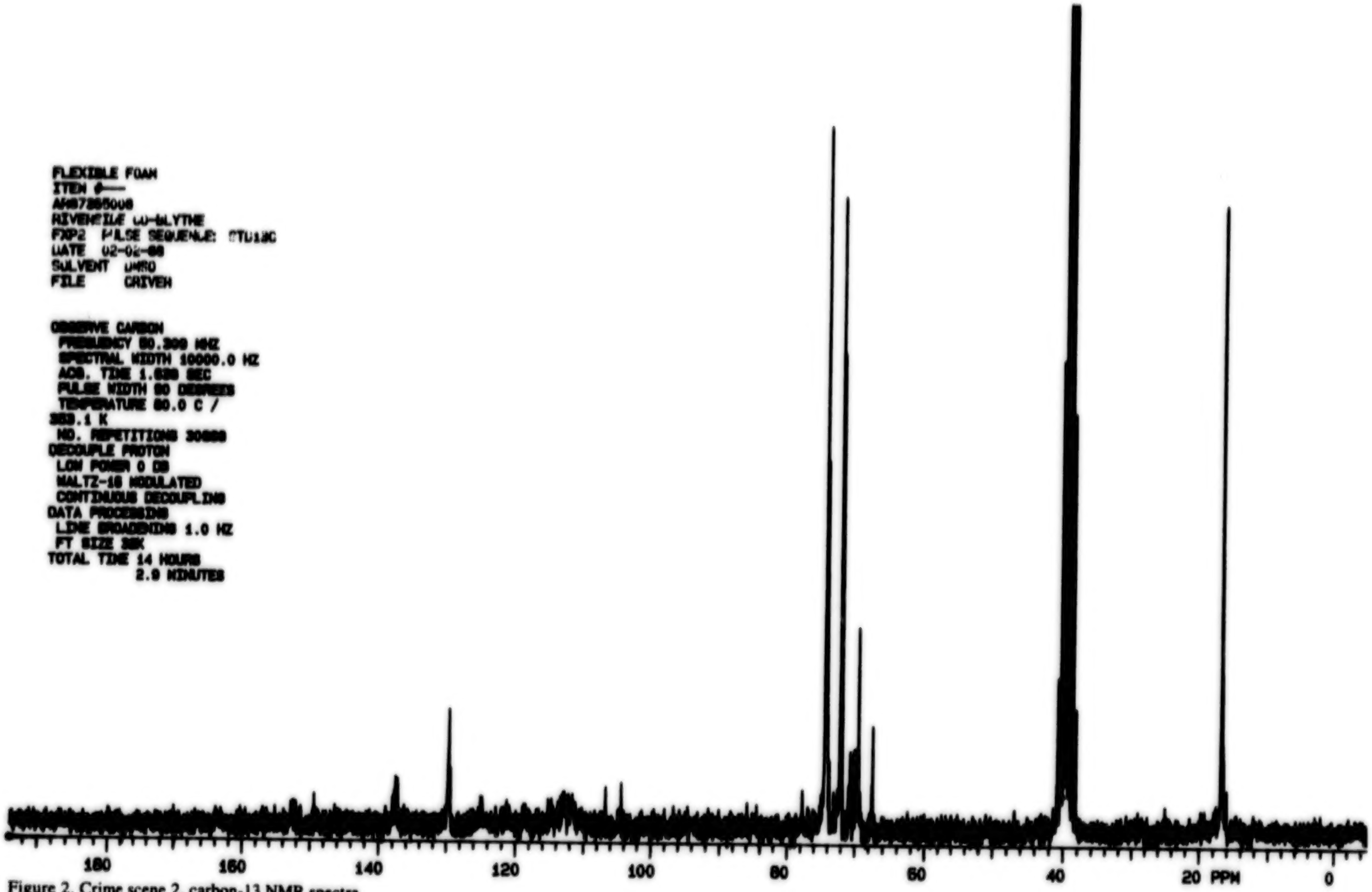


```
FLEXIBLE FOAM
ITEM 9
DR#870944627
LAPD-VNYS
EXP2  PULSE SEQUENCE: STL13C
DATE  02-02-88
SOLVENT  DMSO
FILE     CITEM9

OBSERVE CARBON
 FREQUENCY 50.309 MHZ
 SPECTRAL WIDTH 10000.0 HZ
 ACQ. TIME 1.638 SEC
 PULSE WIDTH 90 DEGREES
 TEMPERATURE 80.0 C /
353.1 K
 NO. REPETITIONS 40002
DECOUPLE PROTON
 LOW POWER 0 DB
 WALTZ-16 MODULATED
 CONTINUOUS DECOUPLING
DATA PROCESSING
 LINE BROADENING 1.0 HZ
 FT SIZE 32K
TOTAL TIME 18 HOURS
           12.3 MINUTES
```

Figure 1. Crime scene 1, carbon-13 NMR spectra.



```
FLEXIBLE FOAM
ITEM #——
AH87285008
RIVERSIDE CO-BLYTHE
EXP2  PULSE SEQUENCE: STD13C
DATE  02-02-88
SOLVENT  DMSO
FILE     CRIVEH

OBSERVE CARBON
 FREQUENCY 50.300 MHZ
 SPECTRAL WIDTH 10000.0 HZ
 ACQ. TIME 1.600 SEC
 PULSE WIDTH 90 DEGREES
 TEMPERATURE 80.0 C /
353.1 K
 NO. REPETITIONS 30000
DECOUPLE PROTON
 LOW POWER 0 DB
 WALTZ-16 MODULATED
 CONTINUOUS DECOUPLING
DATA PROCESSING
 LINE BROADENING 1.0 HZ
 FT SIZE 32K
TOTAL TIME 14 HOURS
          2.9 MINUTES
```

Figure 2. Crime scene 2, carbon-13 NMR spectra.

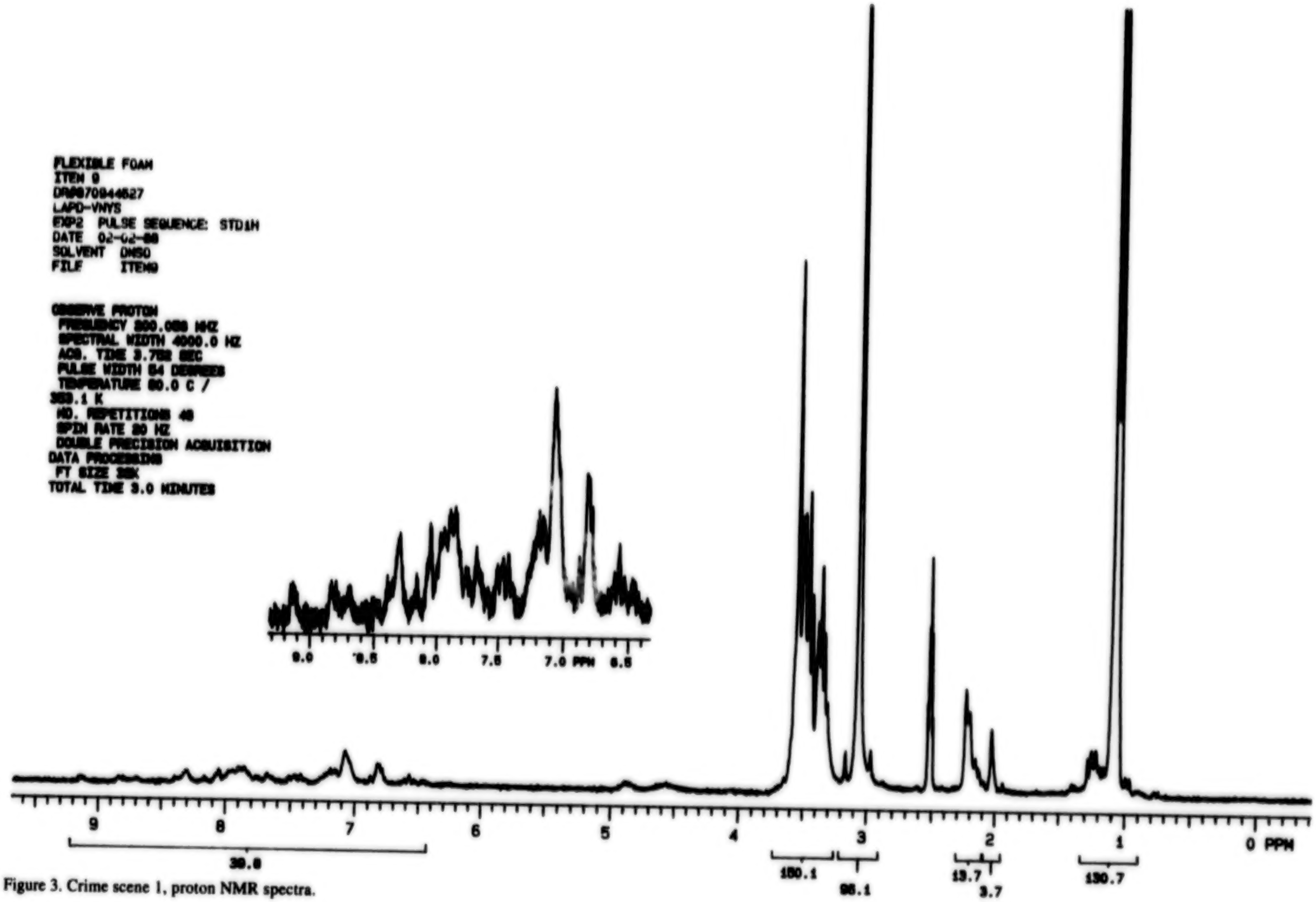
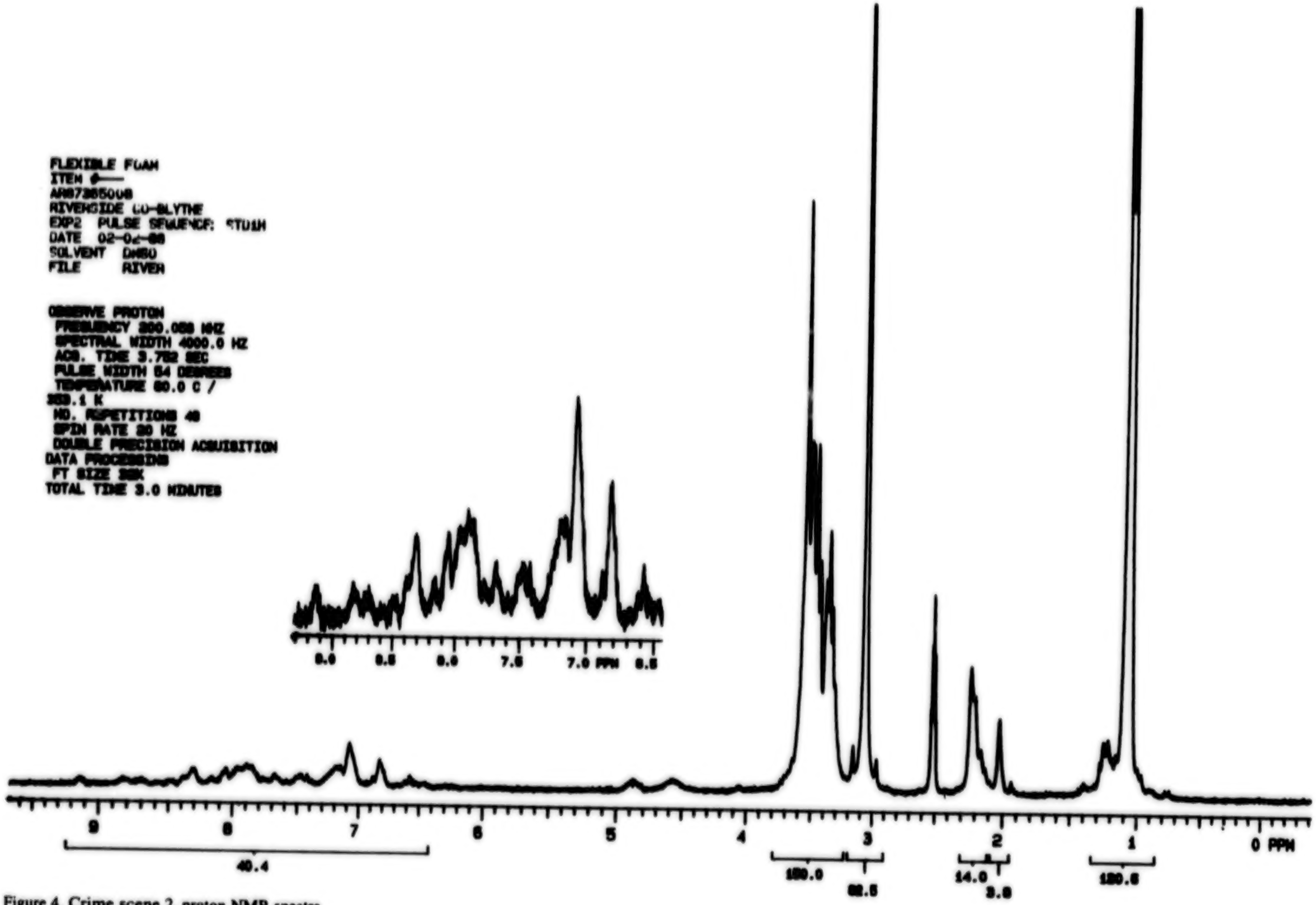


Figure 3. Crime scene 1, proton NMR spectra.



FLEXIBLE FOAM
ITEM #—
AR8735500B
RIVERSIDE CO-BLYTHE
EXP2 PULSE SEQUENCE: STD1H
DATE 02-02-88
SOLVENT DMSO
FILE RIVER

OBSERVE PROTON
FREQUENCY 300.058 MHZ
SPECTRAL WIDTH 4000.0 HZ
ACQ. TIME 3.752 SEC
PULSE WIDTH 64 DEGREES
TEMPERATURE 80.0 C /
353.1 K
NO. REPETITIONS 48
SPIN RATE 20 HZ
DOUBLE PRECISION ACQUISITION
DATA PROCESSING
FT SIZE 32K
TOTAL TIME 3.0 MINUTES

Figure 4. Crime scene 2, proton NMR spectra.

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A NEURAL NETWORK METHOD FOR PATTERN RECOGNITION Of CHROMATOGRAPHIC SIGNATURE PATTERNS OF FORENSIC TRACE EVIDENCE

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Raleigh, North Carolina

J. W. Watterson

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Research Triangle Park, North Carolina

The processing of forensic evidence such as arson, toxic waste, drugs, etc., is typically accomplished by visually comparing unique chromatographic signature patterns of the trace evidence with a signature pattern of a known reference. This approach to pattern recognition of forensic trace evidence is both time consuming and inaccurate to the extent that no information is available on the probability of false detection. An alternative technique such as the neural network was used to compare signature patterns rapidly. The neural network was utilized for pattern recognition of signature patterns of differing illicit cocaine samples containing trace amounts of impurities found in the coca plant and from manufacturing processes.

MATERIALS AND METHODS

A Chromatographic Impurity Signature Profile Analysis (CISPA) (Casale 1991) was used to produce quantitative chromatographic signature patterns (Figure 1) of fourteen known coca alkaloid impurities as unique variables. The qualitative and quantitative data obtained from over 300 differing patterns(different batches of cocaine) were used as references to train the neural network (Watterson 1990) for pattern recognition (Figure 2). In one experiment five randomly selected duplicate exhibits (replicate analysis data) were then applied to the pattern recognition program to determine if matches would be recognized. Additionally, five exhibits from the same batch, each exhibit consisting of five replicate samples, were tested against the trained neural network.

RESULTS AND CONCLUSIONS

All patterns from each experiment were correctly recognized and matched with no false positives. Neural network pattern recognition appears to be a reliable means of establishing common source identity. Results of this preliminary study using differing batches of cocaine show tremendous promise as an attractive pattern recognition method for processing chromatographic profiles of all types of forensic trace evidence.

REFERENCES

Casale, J. F. and Waggoner, R. W. (1991). A chromatographic impurity signature profile analysis for cocaine using capillary gas chromatography, J. Foren. Sci. 36:1312–1330.

Watterson, J. W. (1990). An optimum multilayer perception neural receiver for signal detection, IEEE Trans. Neural Nets. 1:298–300.

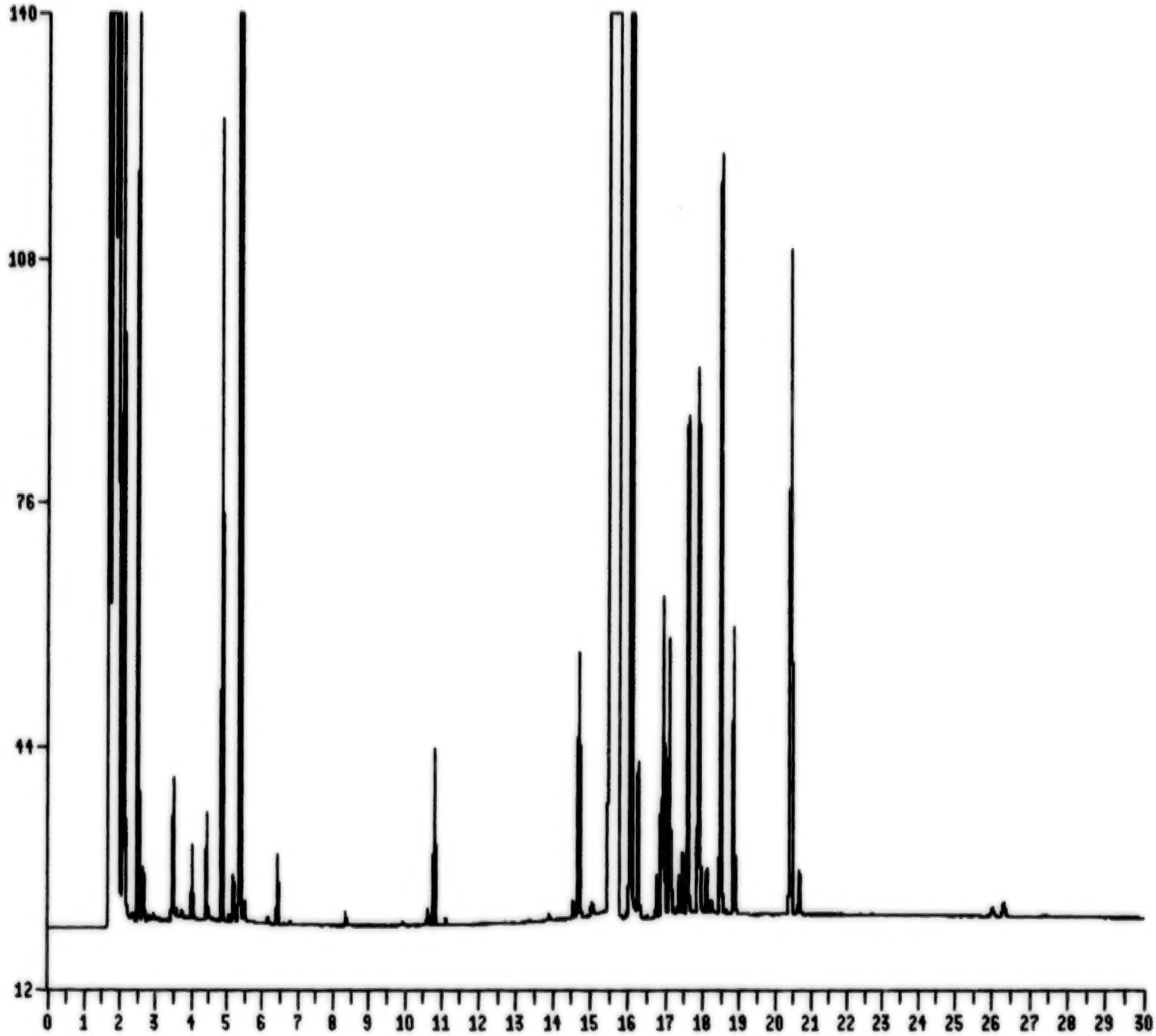

Figure 1. A typical gas chromatographic impurity signature pattern of cocaine.

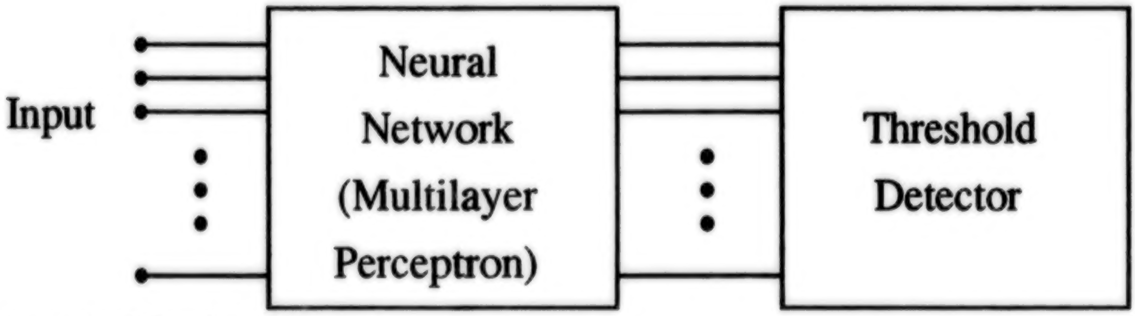

Figure 2. Neural Network Architecture.

TRAINING IN THE FORENSIC SCIENCE SERVICE

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The Forensic Science Service (FSS) contributes to the effective operation of the Criminal Justice System by providing expert scientific support in the investigation of crime, and impartial evidence to the courts.

In April 1991 the FSS became an Executive Agency within the Home Office. To achieve this a radical reorganization of the structure of the FSS has taken place. The operational laboratories have been reorganized along functional lines, with caseworking teams, each headed by a team leader supported by a role-based management structure. This consists of a Director to provide high-level strategic overview; a Forensic Resource Manager responsible for the service output two or three Forensic Service Managers responsible for marketing the service and liaison with the customers; and a Business Manager responsible for local budgetary control, and personnel and administration matters.

This new style of operation for the FSS has meant changes to the way services are delivered to their customers, and to the structure and system.

The senior management team has also been restructured on corporate lines and consists of; the Director General, and Heads of Marketing, Operations, Research, Quality Management, Personnel and Administration, and Management Services.

The new structure supports the corporate style of operation, and is designed to make the FSS more efficient, effective and responsible to its customers needs.

The FSS has contracted to provide a total service to its customers. In order to do this casework is carried out by teams some of which are multidisciplinary. This new style of operation has replaced that based on biology and chemistry departments. Each multidisciplinary team has the skills and performance levels needed to provide a multidisciplinary response and sufficient skills back up to satisfy all reasonable customer demands. A training and development strategy has been prepared to support staff in achieving the required skills, knowledge and competence to carry out their jobs effectively.

Training is carried out mainly in the laboratory using flexible learning packages in all the main evidence types. The packages are undergoing continuous development and improvement and are supported by trained tutors within the laboratory. These in house training packages are supported by centralized courses and workshops.

The FSS has taken the lead in developing a system of National Vocational Qualifications which will be available for all those practicing forensic science. The attainment of qualifications is based on performance and qualifications are related to defined standards of performance which are being developed for all tasks in Forensic Science. This program of qualifications is being carried out in collaboration with organizations independent of the FSS.

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A USE FOR EXPERT SYSTEMS IN FORENSIC SCIENCE

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In order to evaluate the potential of expert systems in the forensic context we have built a prototype system to assist scientists in the interpretation of forensic glass evidence. The aim is to combine recently developed theory and the most up-to-date survey data, with other published and unpublished surveys and to elicit subjective judgements from the user in order to provide intelligent advice.

Recently, there has been an explosion in the number of software products which aim to simulate our routine daily tasks. While it is true that there has been some success at fulfilling this goal in the financial and commercial arena, the encapsulation of rational thought processes, such as those employed to high degree in the forensic world has, for one reason or another, not been explored to the same extent. The main reason for this is probably the lack of formal understanding of the underlying mechanisms of the thought processes which we all take for granted when performing our everyday duties.

To be fair, the software developers have gone some way to assist us by making available products known as expert system shells. These are extremely simple reasoning systems but devoid of knowledge. It is for us to add that knowledge, gained through experience, to produce what is termed a Knowledge Based System (KBS).

The KBS we have developed at the Forensic Science Service, known as CAGE (Computerized Assistance for Glass Evidence) (Buckleton *et al.*) is the result of such a process using the expert system shell CRYSTAL (Intelligent Environments Ltd., Surrey, United Kingdom).

The theoretical framework at the heart of CAGE is that described by Evett and Buckleton (1988) generalized to handle any combination of control and recovered samples.

The appraisal of forensic glass evidence requires inferences to be drawn about the chance of finding the observed evidence under two scenarios:

1 — If the suspect is an innocent member of the public.

2 — If he is, in fact, the person who broke the glass object(s) in question.

Data to assist in the evaluation of the first option is typically drawn from surveys of the population. CAGE will offer data drawn from a survey performed by the Northern Ireland Forensic Science Laboratory, Belfast (J. Mcquillan, personal communication).

A more taxing problem is posed by option 2. The probability of glass being found if the suspect did break the glass object. This is an area in which people operate at an almost subconscious level to great effect. However, getting a computer to tackle the same problem is by no means trivial. We require the probability that glass would have been transferred, retained on the clothing and found. This probability is inevitably heavily case dependent. In view of the scarcity of published data and the variability of real case circumstances it was decided that the best available source of information was the experience of the forensic glass examiners themselves. Hence, subjective judgements are elicited from the user, with the aid of advice from experimentation. These judgements can then be stored for future reference. At the end of a consultation the system analyses those inputs which have most influenced the result. These critical data are reported back to the user so that they can be reassessed to see that appropriate, conservative estimates have been made. The system can associate phrases with numbers in an attempt to express the evidential value agreed upon by the user.

We feel that Knowledge Based Systems have an important part to play in forensic science, providing it is understood that there are particular requirements for these systems peculiar to our field of work. These systems can be an aid to the user presenting him with data and advice, based on judgement and decision.

Systems such as CAGE could also aid consistency of interpretation and reporting and stimulate discussion of these issues.

We have come to realize that one of the greatest assets of our service is the combined knowledge and experience of our scientists. Any method of managing and disseminating this resource must improve the efficiency of operation.

REFERENCES

Buckleton, J. S., Pinchin, R. and Evett, I. W. CAGE: An Experimental Knowledge Based System for Assisting in the Interpretation of Glass Evidence, CRSE Report No. 689.

Evett, I. W. and Buckleton, J. S. (1988). Interpretation of glass evidence: A practical approach, J. Foren. Sci. Soc. 28:388-401.

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THE CHARACTERIZATION OF "COLOR RELEASE" LIPSTICKS

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Avon Products recently introduced a new line of lipsticks called "Color Release®" in which emollients and color are encapsulated in microspheres thus increasing the likelihood of traces being left on contact surfaces due to time release qualities.

METHODS AND MATERIALS

HPTLC was performed on C18 Extract-Elute® solid phase extraction (SPE) columns and 10 x 10 cm Adsorbosil® HPTLC plates with a preadsorbent area (both Alltech, Deerfield, IL). The SPE columns were preconditioned with 2 x 1 ml methanol followed by 2 x 1 ml distilled water. Lipstick samples were extracted with 2 x 1 ml methanol:2N HCl, 10:1. The eluant was probed, mixed, filtered, and transferred to a SPE column contained in a 12 x 75 mm test tube, and centrifuged. The eluant was evaporated, and then reconstituted with methanol:pyridine, 1:1. The extract was then spotted in the preadsorbent zone and migrated in toluene to the top of the plate. The plate was dried in an 80°C oven, redeveloped in toluene:methanol:glacial acetic acid, 65:30:4 (Russell and Welch 1984), dried, and viewed under white and UV (366 nm) light.

A ISI-SX-40 electron microscope with a Tracor Northern TN-5400 x-ray spectrometer and a Polaron E5400 sputter coater was used for SEM/XRD. A thin smear of lipstick was applied to white bond paper (Choudry 1991) and white cotton cloth. Chloroform was applied dropwise to break up the lipstick matrix and then air dried. The samples were located with a stereoscope at 50x. The located microspheres were attached to the appropriate area to an aluminum stud with double-stick tape. Samples were gold sputter coated at 20 mA and 725 V for 2.5 minutes, searched and analyzed at 20 kV with a working distance of 20 mm and a 10° tilt.

A Nanospec Model 105 Microspectrophotometry (MSP) was used. Light smears were made on clean white cotton, a few fibers were teased out, and mounted in XAM Improved Neutral White. MSP conditions were 250 x magnification, 5 x 40 μ slit size, 390 to 730 nm range with a 200 nm/minute scan speed, and a filter setting of 2.0.

A NicPlan microscope with a Nicolet 740 spectrometer was used for FTIR analysis.

RESULTS

The HPTLC analysis provided clear and distinct dye separation while SEM/XRD provided morphological and elemental identification of intact microspheres (Figures 1 and 2). The microspheres contained silicon, chlorine, and magnesium. Four of the 12 Color Release® lipsticks (Endless Garnets, Forever Rose, Lasting Mauve, and Long-Lived Ruby) did not appear to have the abundance of microspheres as did the other eight (Table 1 contains a list of the lipsticks). MSP was able to differentiate the lipsticks. Preliminary results from FTIR are promising.

CONCLUSION

The HPTLC, MSP, and FTIR give a good basis for lipstick comparisons while the presence of intact microspheres appeared to make these lipsticks unique.

ACKNOWLEDGEMENT

We would like to thank Tricia Silva, San Diego Children's Hospital, for her assistance.

REFERENCES

Choudhry, M. Y. (1991). Comparison of minute smears of lipstick by microspectrophotometry and scanning electron microscopy/energy-dispersive spectroscopy, J. Foren. Sci. Sci. 36:366–375.

Russell, L. W. and Welch, A. E. (1984). Analysis of lipsticks, Foren. Sci. Inter. 25:105–116.

Table 1. AVON PRODUCTS "COLOR RELEASE®" LIPSTICKS

Continuous Coral
24 Hour Red
Enduring Sable
Boundless Berry
Timeless Pink
Stayput Salmon
Prolonged Peach
Unsurpassed Wine
Forever Rose
Lasting Mauve
Long-Lived Ruby
Endless Garnets

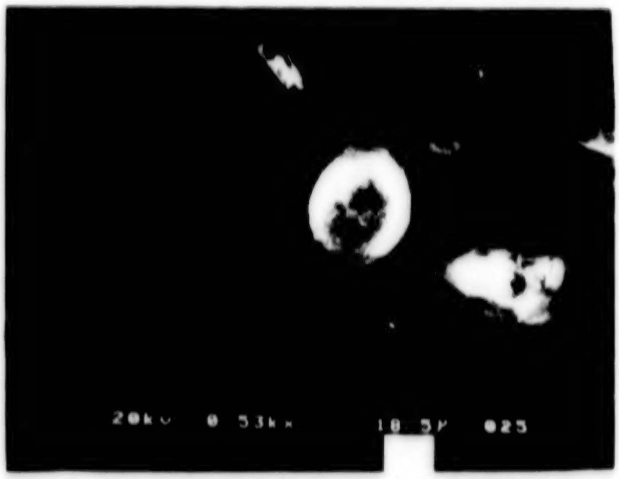

Figure 1. Gold coated microshpere from Avon Continuous Coral Lipstick, 530x magnification.

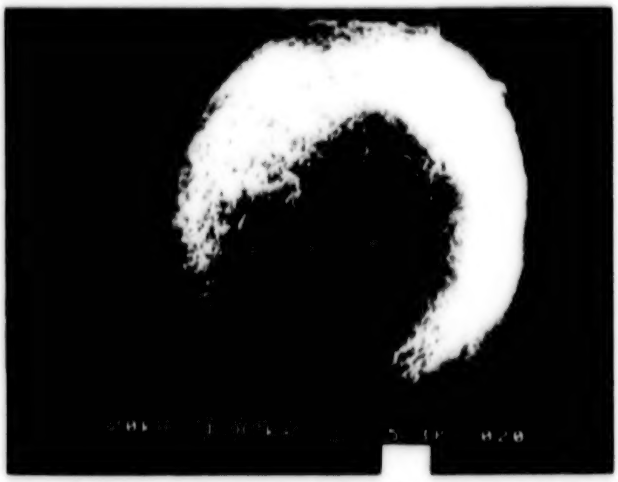

Figure 2. Gold coated microshpere from Avon Continuous Coral Lipstick, 1870x magnification.

DESIGNER EVIDENCE: THE USE OF TAGGANTS AT THE METROPOLITAN POLICE LABORATORY

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A taggant is a device which enables conclusive identification of materials. It may also enable positive identification of any person who has handled or come into contact with it.

The taggants used at the Metropolitan Police Laboratory generally consist of a mixture of identifiers contained within a base material. There are two broad types of taggant base: permanent and transferable. Permanent bases are designed to remain on a surface to which it has been applied, while transferable bases readily transfer to a person or object which comes into contact with it. Although transferable bases have a considerable risk of contamination if used unwisely, they can provide evidence of contact with a tagged item.

The combination of identifiers used in a taggant must be unique so that they give irrefutable evidence. Identifiers can conveniently be divided into four types: U. V. chemicals, colored dyestuffs, rare chemical elements and microparticles.

A taggant can provide conclusive evidence their use has to be carefully controlled. Each and every case, therefore, has to be considered and the taggant designed according to the crime and the circumstances. Experience at the Metropolitan Police Laboratory has shown that there are no simple rules that can be applied to decide what type of base and identifier combination should be used.

For poorly considered cases using an incorrect design of taggant the results will be ambiguous and possibly misleading. The use of transferable taggants is especially critical and monitoring of the scene is of prime importance to prevent the contamination of both the scene and innocent persons.

Four casework examples of taggants were examined where the combination of identifiers and base material used has been designed for a specific set of circumstances. The examples were tagging the seats of a get away vehicle, money used as a ransom in a blackmail case, valuables in repeated thefts from aircraft baggage and coins in a fruit machine.

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THE FORENSIC APPLICATION OF SOME UNIQUELY PREPARED MARKING POWDERS

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Hong Kong

For many years this laboratory has been supplying marking powders as an aid to crime detection, especially in crimes related to blackmail, kidnapping, theft, and corruption. The majority of these operations involve personal transfer of money or other tangible items. Invisible marking of the item prior to handing over to the culprit allows for subsequent positive identification and proof of contact with the marked item.

To serve the above purpose as a marker, the substance used should be:

1 - Minute in size,
2 - Invisible to the naked eye under normal lighting,
3 - Easily applied and recovered, and
4 - Specific in nature.

The marking powders that we use in the laboratory are basically made up of three components (Table 1), each with different characteristics to meet the above stated criteria. Lycopodium is selected as the base of the powder because of its minuteness and its honeycomb structure is an excellent substrate for the addition of specified compounds. It is also easily recognizable under the scanning electron microscope. Rare earth compounds are used as the specified of the marking powder because of the large selection available, and more importantly, because they are not commonly encountered in everyday life. Short wave UV-excited compounds and long wave UV-excited zinc sulphide are added to the marking powder as the indicator of the location of the marking powder. These compounds are invisible under normal lighting conditions but show up distinctly using a UV fluorescent lamp.

The preparation of the marking powder involves a simple procedure as indicated in Table 2. Marking powders are easily applied by gently rubbing the surfaces and edges of the item with the powder. The recovery of the marking powders from the culprit's hands, clothing and other items is done by taping with clear adhesive tapes. These are subsequently examined in the laboratory for the presence of the marking powders by a scanning electron microscope incorporated with an energy dispersive X-ray analyzer (SEM-EDX).

Table. 1. THE CONSTITUENTS OF THE MARKING POWDERS.

Base —	Lycopodium Power
Specifier —	Rare Earth Compounds
Indicator —	Short Wave UV-excited Compounds and Long Wave UV-excited Zinc Sulfide

Table 3 is a summary of all the cases handled by this laboratory since 1988 which involved the use of marking powders. In the cases which led to a subsequent arrest, it was found that in each instance, the marking powder used was recovered from the arrested. This 100% recovery rate indicates the success of the marking system used.

A recent case of blackmail illustrates the use of the marking powder: Protection money of 5000 Hong Kong dollars was demanded from the owner of a jewelery shop. The money was treated with some marking powder before it was handed to the culprit by the victim. Police laid an ambush outside the shop and the culprit was subsequently apprehended. Marking powder agreeing in composition with that on the treated money was recovered from the hands and trouser pockets of the arrested person.

Table 2. PREPARATION OF THE MARKING POWDERS.

1 — 0.1 gm of a rare earth compound is dissolved in 50 ml of deionized water or absolute alcohol. 4 gm of lycopodium powder are added to the solution and the mixture is mixed thoroughly in an ultrasonic bath for 30 minutes;

2 — The mixture is dried on a water bath and the dried mixture is subsequently stirred into 25 ml of toluene containing 0.3 gm of a glue extracted from 'TESA' adhesive tape;

3 — Excess glue solution is filtered off and the filtered powder is dried in an oven at 60°C for 1 hour;

4 —The dried powder is mixed with 0.1 gm of a pre-ground short wave UV-excited compound and is shaken mechanically to homogeneity;

5 —The doped lycopodium powder is mixed with long wave UV-excited zinc sulfide in the ratio of 1:1 to complete the preparation of the marking powder.

Table 3. CASES HANDLED INVOLVING THE USE OF THE MARKING POWDERS.

Year	1988	1989	1990	1991 (Jan–Mar)
Number of Requests	20	11	18	9
Number of Requests with Arrest	1	1	3	4
Number of Arrests with Successful Recovery of Marking Powder	1	1	3	4

The combination of lycopodium doped with mixtures of rare earths and short and long wave UV-excited compounds, specially prepared in the laboratory is highly specific in nature. Therefore a positive recovery of the powder from the culprit often constitutes strong evidence of contact between the culprit and the item treated with the marking powder.

AN INTERACTIVE GRAPHIC DATABASE FOR USE IN THE IDENTIFICATION OF POLLEN GRAINS

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Using an Apple Macintosh computer and working in the Hypercard programming environment, I designed and constructed a prototype user-friendly database which is designed to assist microscopists in the identification of pollen grains.

Pollen grains are generally identified by classifying a number of their morphological features, then using this information to navigate through some sort of identification key. The number, type and arrangement of the apertures (openings) on the surface of pollen grains represents the most important morphological feature with respect to their identification. These apertures can be of three basic types; round pores, elongated furrows, or a combination of the two (a round pore inside of an elongated furrow). The apertures can vary in number from one to more than six, and can either be arranged along the equator, or scattered over the entire surface of the grain. The fine patterned appearance of the surface of most pollen grains is known as the sculpturing. Although this sculpturing is often extremely fine, its general pattern can usually be appreciated with the light microscope (oil immersion) and classified as belonging to one of a limited number of basic forms. Closely related to the surface sculpturing is the tectum structure. Whether the outer surface of a pollen grain has a tectum (literally a roof), which is supported by minute columns, is an important morphological characteristic. A grain can be classified as tectate (having a full tectum), semitectate (having a partial or perforated tectum), or intectate (having no tectum structure). Size is another feature of pollen grains that is often used in their identification. Although the size of pollen grains can show considerable within-species variation, and is also somewhat influenced by the medium in which the grains are mounted for microscopic observation, this characteristic, if used in fairly broad categories, can still be important for identification purposes. The general shape of pollen grains can also be a useful identification feature. Since the actual three-dimensional shape of the grains is difficult to glean from the two-dimensional images of the light microscope, general shape classifications, such as the P/E index, are often used. The P/E index of about 1.0 would indicate a spherical grain, while indices of greater than and less than 1.0 are indicative of prolate (tall and thin) and oblate (short and fat) grains, respectively.

The characteristics of pollen grains just described, along with some less common features of the aperture structure, represent the major criteria used in their identification. Unless it is extremely unusual, no single feature is sufficient to make an identification. It is rather the combination of a number of these morphological characteristics which sets apart the grains of an individual species, genus, or family. In using the computer database discussed here, the user, through a series of graphic prompts and choices, classifies their unknown grain with respect to one or more of these morphological features. The database then searches its files for all candidate grains which share the particular combination of morphological characteristics specified by the user. The family, genus, and species name of each of the possible candidate grains are then listed in a scrolling window. From this list, the user can access scanned-in images and detailed descriptions of the individual pollen grains. Alternatively, the user can browse through the images and descriptions for all of the grains in the candidate list and eliminate the grains from the list that do not match their unknown as they go along. Depending on the results of the first search, the user may also decide to specify additional morphological characteristics of their unknown grain, thereby narrowing the search, and shortening the list of possible candidates.

This database, especially with the limited quantity of data that it currently contains (images and descriptions for approximately 350 grains), is by no means a panacea for the identification of pollen grains, nor is it a substitute for formal study in palynology. In my opinion, however, this type of system represents an efficient way of organizing and using information that offers several distinct advantages over the conventional approach. One of the primary advantages of the computer-based system lies with the level of flexibility in the choice searching parameters. In other words, the database does not force the user to make decisions about their unknown that they may not be sure about, given that certain morphological features may be obscure and that pollen grains are not always found in perfect condition. another advantage that the computer-based identification system has over the dichotomous key approach is that the computer database is open-ended and expandable. Although no single identification key or computer database can ever approach representing every variety of pollen grain, new grains, from many different sources, can be added to the computer system at any time, and be included in the next search. In addition, the graphic interface of this database provides an imaged-based classification of the various morphological features, thereby limiting the use of the sometimes confusing and inconsistent terminology of pollen morphology that confronts the microscopist who may only rarely have occasion to attempt a pollen identification.

ON THE POSSIBILITY OF ACCIDENTAL CONTAMINATION OF GSR: A STUDY OF THE DIFFUSION AND PERMANENCE IN THE ENVIRONMENT

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For some time the issue of the possibility of accidental contamination of Gun Shot Residue (GSR) has been raised in Italy. In particular, the uncertainty of a contamination from police officers taking samples is often proposed. Moreover, the theoretical possibility exists that in some places there are particles of ancient shots present, which may settle on the hands or on the clothes of particular subjects for reasons independent of a recent shot.

In this study the results of the research of GSR on samples taken from several surfaces where the possibility of a deposit of GSR is greater, as well as hands and garments of people theoretically exposed to contamination from non-recent shots, are presented. The samples were obtained with conventional studs covered with adhesive tape on the following surfaces:

1 - Hands of 20 persons arrested for reasons different from shooting and kept in the premises of the criminal police;
2 - Premises, furniture and garments within police stations (10 samples);
3 - Several surfaces in the bar of the Turin rifle range (counter, front door, etc.) on the day of maximum attendance by marksman and on the day following the weekly closing for control (10 samples);
4 - Houses of two sports marksmen (10 samples);
5 - Hands of 10 Carabinieri (Policemen) who had not used fire-arms recently.

The analysis of the samples was carried out in automatic search by SEM-EDX technique (CAM-SCAN/TRACORS). The samples on which at least a GSR exclusive particle was found were considered positive.

Results were negative in all cases but the following:

1 - Houses of sports marksmen; safe were firearms are kept, closets where clothes used in the firearms range are put back, bedroom where reloaded (the sample taken in the living-room was negative since firearms are rarely handled here);
2 - Bar of the Turin firearms range; counter, a glass used by a sports marksman (controls carried out after the cleaning of the premises were negative).

The fact that all samples taken in the premises linked to the police stations were negative suggests that the danger of casual contamination of the arrested persons is very limited or even non existing.

On the contrary, the contamination of premises and objects closely related to sports marksmen and their firearms is possible and this event is not only a theoretical one. To this regard it is necessary to take into account that these people shoot many cartridges.

All of this obliges us to be very careful in considering the positive results of these investigations as a real proof of shooting. As a matter of fact, in some particular cases, the concrete possibility exists that both hands and clothes can be accidentally contaminated from GSR coming from even old shots.

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THE ELEMENTAL COMPOSITION OF BULLET WIPINGS ON CLOTH AND ITS RELATIONSHIP TO SUSPECTED AMMUNITION

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On September 6, 1989 an Immigration and Naturalization Service (INS) Officer was shot and killed during an undercover investigation in Fresno, California. The suspects in the investigation were involved in the selling of illegal immigrants for labor. While attempting to arrest these suspects, numerous gunshots were exchanged and an INS Officer was fatally wounded. The fatal bullet had entered the lower middle back and exited the lower middle abdomen. During the investigation, the question arose as to who actually fired the fatal round.

The focus of this paper is the examination of the bullet hole wipings on the victim's shirt and their comparison to the suspected weapon/ammunition combination. Table 1 provides a listing of the weapons and ammunition of each armed subject in this case.

METHODS

The first series of tests were designed to look at any differences in bullet wipings because of different ammunition/weapon types involved in this case. White polyester cloth squares were used as test targets. Each weapon was cleaned with a dry patch prior to the test shot. All test shots were conducted at a distance of 0.6 m between the muzzle and target. This distance approximated the gunpowder pattern on the victim's clothes. Table 2 lists the sequence of the first series of tests.

A portion of the bullet wipings around the hole was cut from each target, mounted on a carbon disc, and carbon coated. These were then examined with an Hitachi Scanning Electron Microscope with a Tracor Northern Energy Dispersive X-ray Detector. Both the appearance and elemental composition of the wipings were examined. Several 20 μ windows were selected for XRF analysis.

A second series of tests were designed to show reproducibility of the results and the effect of alternating lead and jacketed bullets in a shooting sequence. The barrels were not cleaned between shots. The target and shooting distance remained the same.

Table 3 listed the sequence of these tests. All results were then compared to the analysis of the victim's shirt.

RESULTS

Significant reproducible differences were found between basic ammunition types. Bullets with grease in

Table 2. SEQUENCE OF THE FIRST SERIES OF TESTS.

Test Targets:

Test 1 — .357M Ruger, Security Six with Federal LSWC Ammunition

Test 2 — .357M Ruger, Security Six with Midway SJHP Ammunition

Test 3 — .357M Ruger, Security Six with Commercial Reload (LSWC)

Test 4 — .357M Smith & Wesson with Federal SJHP

Test 5 — .380A Llama with Federal FMJ

Test 6 — 9mm Glock with Winchester Silvertip

Table 1. WEAPON AND AMMUNITION USED IN ACTUAL CASE

Subject	Weapon	Ammunition
INS Officer #1	9mm Glock	9mm Winchester Silvertip
INS Officer #2	9mm Glock	9mm Winchester Silvertip
INS Officer #3	.357M Ruger	.357M Winchester - Semijacket, Hollow Point (SJHP)
INS Officer #4	.357M Smith & Wesson	.357 Federal Semijacketed Hollow Point (SJHP)
Suspect #1	.380 Llama	Federal Full Copper Jacketed .380 AUTO (FMJ)
Suspect #2	.357M Ruger - Security Six	a. Federal Lead Semiwadcutter (LSWC)
		b. Commercial Reload Lead Semiwadcutter (LSWC)
		c. Midway Semijacketed Hollow Point (SJHP)

their grooves may leave this material on fibers of the fabric (Figure 1).

The elemental analysis of the bullet wipings separated these targets into three basic groups. They are as follows:

1 - Lead bullets - primarily lead was detected in wipings.

2 - Semijacketed bullets with exposed lead nose - primarily lead with lesser amounts of copper was detected in the wipings.

3 - Full metal jacketed bullets (copper or nickel/copper) - primarily primer components of lead, barium, and antimony were detected in the wipings. Using a 20 μ area for the EDX analysis, no significant difference between copper jacketed and silvertip ammunition could be detected. Only with a Spot analysis or substantially smaller windows, nickel could be detected in the silvertip test targets. Varying the sequence of shots through the same barrel did not significantly change the elemental profile of the test target bullet wipings.

Table 3. Sequence of second series of tests.

9mm Glock:
Test 1 — Silvertip Bullet
Test 2 — Copper Jacketed Bullet
Test 3 — Lead Round Nose Bullet
Test 4 — Silvertip Bullet
Test 5 — Copper Jacketed Bullet
Test 6 — Silvertip Bullet

.380 Llama:
Test 1 — Copper Jacketed Bullet
Test 2 — Copper Jacketed Bullet
Test 3 — Silvertip Bullet
Test 4 — Lead Round Nose Bullet
Test 5 — Copper Jacketed Bullet

CONCLUSION

These results confirmed other analytical and reconstructive information which indicated that the suspect firing the .380 Llama was responsible for the death of the INS Officer.

This case study shows a potential for discriminating between bullet types based on the elemental composition of the resulting wipings.

ACKNOWLEDGEMENT

I would like to acknowledge the contributions of John Hamman, Criminalist, California Department of Justice, who was case criminalist and who prepared all the test targets for this study.

Figure 1. Photograph of SEM results.

HAND GRENADE AND PRIMER RESIDUE PARTICLES

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Primer particle identification is a well-founded and widespread method used for screening and identifying suspects in shooting incidents. It may be expanded and used in other cases as well. An example of this is the case of hand grenade throwing which occurs in both terrorist attacks and crime related reprisals. This expansion inherently requires a more general term than gunshot residues (GSR) or cartridge discharge residues (CDR) and was termed by us primer discharge residues (PDR).

Finding primer residue particles in grenade throwing incidents is not trivial as there is a basic difference between the act of shooting and that of throwing a grenade. In the case of shooting, the person holds the gun at the time of firing; in the usual method of grenade throwing, the primer is detonated after the grenade leaves the hand of the thrower.

MATERIALS AND METHODS

Training (fitted with only the detonator mechanism) IMI (Israel) #26 and Soviet made F-1 hand grenades were studied and used in this work. The act of throwing a hand grenade was video-taped using a JVC S-1000 Super-VHS camera.

Eleven test throwings were carried out, both outdoors and in a closed range. In all the test throwings, blanks were sampled from the participants before the grenade was thrown. Each subject was sampled twice, immediately after the throwing, using Scotch Brand Tape #465 (3M Company, St. Paul, MN) adhesive-backed 2.5 cm aluminum stubs. One stub was used to sample the subject's arms and hands. The other stub was used to sample the subject's upper torso, facial area and hair.

The stubs were then examined using a CamScan IV (Cambridge, England) scanning electron microscope equipped with a Seforad (Israel) Li/Si detector and a Tracor-Northern (Middleton, WI) TN-5500 EDX analysis system. This system is coupled with the CamScan/ Metropolitan Police automatic particle analysis system, Keeley and Nolan (1986).

RESULTS AND DISCUSSION

Figure 1 is a typical frame taken from a videotaping of one hand-grenade throwing test. In close proximity to the thrower's hand the plastic-wrapped grenade is seen, and evolving from it, a smoke cloud. The same was observed in all the other tests.

Figure 1. Particles cloud near the grenade thrower's hand.

Data from the eleven test throwings performed, nine outdoors and two indoors, are tabulated in Table 1. In eight of the eleven, primer discharge particles were found on at least one of the sample stubs taken from the thrower. Six of the positive findings were from outdoor throwings and two were from the indoor ones. While outdoor throwings are more prevalent in regular case work, cases of indoor throwings such as in stairwells or apartment buildings, may also be encountered.

In the eight instances of positive results, between one and thirty PDR particles were found in each. It must be remembered, however, that samples were taken immediately after the throwings. One would expect the particles from hand grenades to behave similarly to those from firearms in respect to their duration of adherence (Wallace 1980).

The feasibility of detecting primer discharge residue (PDR) using the SEM/EDX method on suspects in hand grenade throwing incidents was verified.

REFERENCES

Keeley, R. H. and Nolan, P. J. (1986). Automated particle analysis, Metropolitan Police Report and Report to Interpol Meeting.

Wallace, J. (1980). Firearms Ammunition - Chemical Aspects, Metropolitan Police Forensic Science Laboratory SEM/MPA Firearms Discharge Residues Training Manual, p. 91.

Table 1. RESULTS FROM TEST THROWINGS

Test No.	Hand-grenade	Indoor (i) /Outdoor (o)	Sample from Hands/Arms*	Samples from Head/Torso*	Remarks
1.	IMI #26	o	5	—	
2.	IMI #26	o	—	1	
3.	IMi #26	o	—	3	Many Sn Prt. on Hands
4.	IMI #26	o	—	—	Many Sn Prt. on Hands
5.	IMI #26	o	—	—	
6.	IMI #26	i	3	2	Many Sn Prt. on Hands
7.	IMI #26	i	—	2	
8.	IMI #26	o	—	—	
9.	IMI #26	o	17	2	9 'Pure', 8 & Sn
10.	F1	o	30	—	Bi & Cr Part.
11.	F1	o	1	1	

DETERMINATION OF TAMPERING OF HEAT-SEALED PLASTIC BAGS

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Close microscopic examination of the heat-seal on plastic bags will disclose evidence of tampering (opening and resealing) as well as the identity of the heat-sealer involved. Characteristic impressions are left behind on the heat-sealed bag in the form of random fiber impressions from the heated Teflon tape of the sealing unit. The weave pattern making up the Teflon cloth leaves a characteristic criss-crossing pattern on the bags when sealed. To orient the bags on the comparison microscope a close observation must be made first to determine which side of the bag was in contact with the fiber portion of the sealer unit. Once this has been done a reference mark can be made on the bag for measurements. Some sealer units develop hot spots at the ends of the bar and cause burns in the bags. These burns make great reference markings. Pressure exerted, heat settings, and time held in unit will all affect the type of seal obtained. For this reason a series of test seals at different sealing times will give good exemplars for comparison to the suspected heat-sealed bag. This is done for each sealer that may have been used for resealing of a bag. Mark which end of the test seal was oriented to the tape and hinge. A comparison microscope is used for the testing. The scope used consists of two polarizing light microscopes coupled with an optical bridge. The mechanical stages were modified to hold matte black aluminum plates, approximately 13 x 18 cm in size. These replace the standard slide holding apparatus. Top lighting, provided by twin, bifurcated, fiber optics is used instead of transmitted light for these examinations. The specimens are held in place using double sided sticky tape placed above and below the area observed. Place the Teflon tape, sealed side up, and then rotate the stages slightly to align the observed patterns (Figure 1).

The difficult part of the exam is to orient the pattern and compare the impressions to the set of known impressions. Once the exemplar or test seal is oriented on one of the stages of the comparison microscope, the suspected bag is placed on the other stage. The reference mark from the hinge side is positioned similarly to the reference mark on the known exemplars. A close examination of the pattern under the comparison microscope reveals the individual twist patterns in the threads making up the fabric of the cloth. Upon closer examination it becomes obvious that the patterns assume a random orientation with some threads crossing at different angles and causing unique impressions on the heat-sealed bag. Set up the optical bridge so the images from both stages are superimposed over each other. This procedure allows the examiner to align the seals for comparison. The light sources can be adjusted for better contrast. One stage at a time is moved to look for patterns which are similar between the different seals. Once an area is found with seals oriented similarly, both stages can be moved in unison to show that the patterns remain similar across the length of the seal. The examiner will have identified the sealer used to reseal the bag at this point.

The examiner may have to reorient the sample depending on which side of the sealer the bag was sealed on. It may take some time to find the initial starting point. However, once a starting point has been found, everything else falls into place. The examiner should

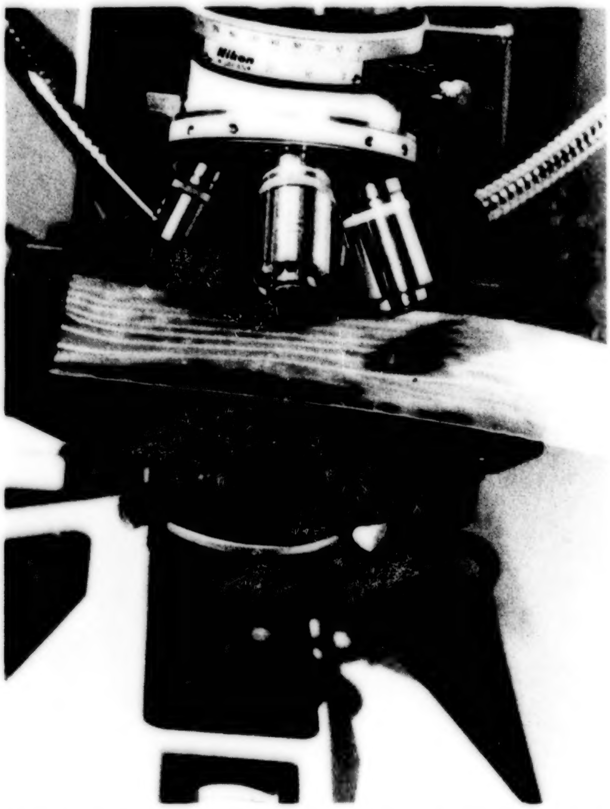

Figure 1. Orientation of heat-sealed plastic bag on modified stage of comparison microscope.

also be careful to note any overlaps of plastic or gaps along seal. These are indicative of opening of seal and resealing. Figure 2, 3, 4, and 5 provide examples of examination at 100 X.

Note: If sealer tapes have been changed since sealing a bag. It will become necessary to find a bag that was sealed during the same time frame and use it as an exemplar.

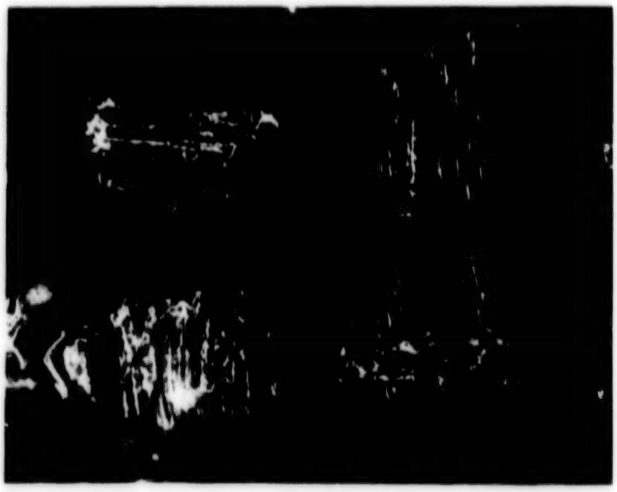

Figure 2. 100X view of test seal on left stage.

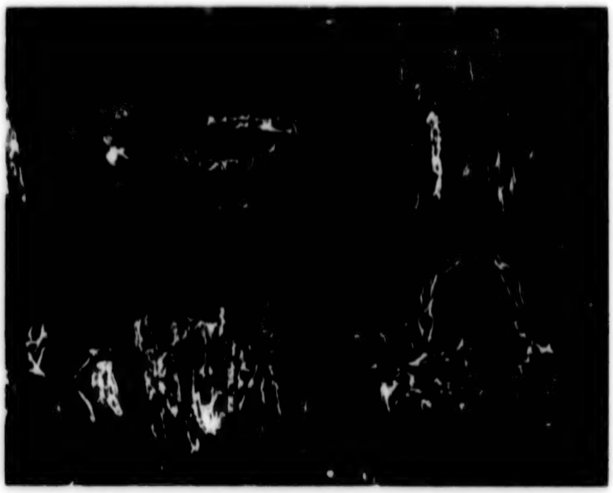

Figure 3. 100X view of seal on right stage.

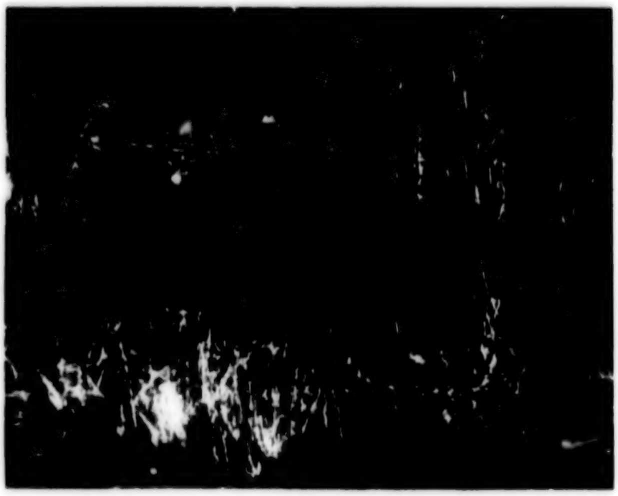

Figure 4. 100X offset view of seals on both stages.

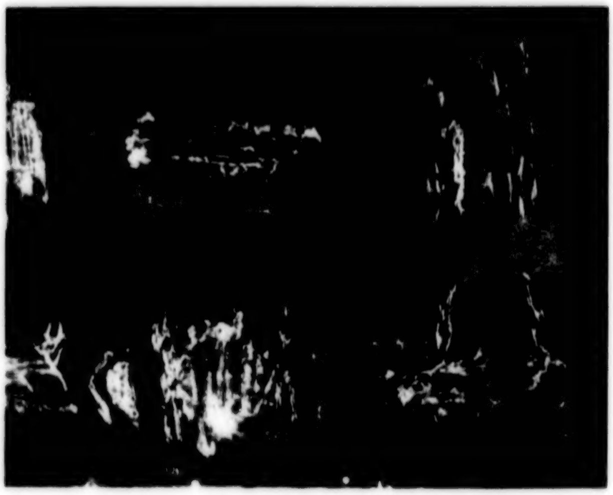

Figure 5. 100X view of overlapping seals.

DISCRIMINATION OF SOIL MATERIALS USING IDENTIFICATION OF MICROFOSSILS

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Soil materials on the surface of earth are decreasing owing to urbanization, however, a large quantity of sands are being used for various purposes. Sands, therefore, become important soil materials in large cities. Most of these sands contain microfossils and the kinds of microfossils found in them are various. Discrimination of sands using identification of microfossils contained in them was examined to determine whether identification of microfossils would be useful for discrimination of soil materials in criminal identification. An effective example of expert evidence of identification of microfossils applied to discrimination of soil materials for criminal investigation is introduced.

EXPERIMENT

There were 22 different sands used in this study. They were provided from areas where production facilities were known, and additional samples were provided from other areas around Tokyo. These 22 sands were comprised of 17 mountain sands and 5 river sands. Those samples were obtained from traders, treating building materials and concrete in Tokyo. The producing areas are Chiba, Kanagawa, Ibaragi and Saitama Prefecture adjoining Tokyo Metropolis.

Samples were sifted in a 200-mesh screen and microfossils in sands remaining on the screen were observed through a microscope at 40x. The kinds of microfossils found in these sands were foraminifera, bryozoa and so on. The size of those microfossils is hundreds of microns. Sands sifted out through a screen were used as samples for observations of diatoms through a microscope at 1000x. The size of those diatoms was dozens of microns. Approximately 5-150 g samples were used in this experiment in order to identify 200 valves of foraminifera or diatoms.

RESULTS

The results of this experiment showed that all 17 mountain sands of the 22 sands examined contained the microfossils of marine living things. The frequency of production of foraminifera was higher than that of any other microfossils found in mountain sands. Comparison on the kinds of microfossils and the species of foraminifera found in these 17 samples could be classified into 13 groups. Species of foraminifera found in those samples are existing species living in shallow sea except one extinct species. So, it is presumed that those mountain sands accumulated in shallow sea at an age earlier than Pliocene, about two million years ago.

On the other hand, dead bodies of diatoms inhabiting fresh water were found in one of the 17 mountain sands and 5 sands from the Tone River. Comparison of the species of diatoms found in 6 samples could be classified into 4 groups and discriminated among sand from downstream, that from middle river and that from branch of river.

Accordingly, identification of microfossils found in these 22 sands could be classified into 16 groups and provided us with the information on the accumulation of sands in the environment.

EXAMPLE OF EXPERT EVIDENCE

The case of a bank robbery, where 3 hundred million yen were stolen, occurred in Tokyo in 1986. At that time, we had the opportunity to provide expert testimony on the soil materials that were examined. Samples were soil materials left in the car used by the criminals and 1063 soil materials gathered at the scene of crime and its vicinity in Tokyo Metropolis. As result of the examination of soil materials left in car used by the criminals, no peculiar mineral was found. The soil materials left in car were sands, composed of quartz, feldspar and so on. However, a bryozoa was found. This same species of bryozoa, as the bryozoa found in soil materials left in car, could be found in only 11 samples of 1063 samples. One of the places where those 11 samples were gathered corresponded with the residence of criminals. This result became important corroborative evidence for the solution of this case.

CONCLUSION

Identification of microfossils such as foraminifera, bryozoa and so on is very useful for the discrimination of the sands from the mountains made by the upheaval of the bottom of the sea. The identification of diatoms is very efficient for the discrimination of river sands.

Accordingly, identification of microfossils is considered to be very useful for the discrimination of soil materials for criminal investigation.

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A SIMPLE MINERALOGICAL SOIL ANALYSIS METHOD USING DISPERSION STAINING WITH FIVE OILS

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Most forensic scientists do not have a strong background in geology or optical mineralogy. As a result, soil examination is not performed in many crime laboratories, while other laboratories may rely solely on color and grain size distributions. Although these are important characteristics, it should be stressed that their greatest value, perhaps, is for exclusionary purposes. A relatively quick and simple scheme for examination of forensic soil samples has been developed. This scheme places primary emphasis on dispersion staining (McCrone *et al.* 1979), but also uses other optical properties, such as color, birefringence and relief (Kerr 1977).

The six step method begins with a non-destructive examination with a polarizing microscope of a small sample of sieved, washed and dried soil mounted in xylene. This examination is used as a screening step which looks at the color, birefringence, and for the presence of magnetic particles or isotropic minerals having a refractive index less than xylene (1.497) such as fluorite and opal. In this step and subsequent steps, counts or approximate counts of the mineral distribution are made (Graves 1978). This is facilitated by using a cross line eyepiece which permits checking for minerals one quadrant at a time. If sample size permits, six or eight different fields are observed allowing approximately 300 grains total to be analyzed. The soil may be dried and recovered, if necessary, for subsequent steps. Steps 2 through 6 consist of examination in a series of five different refractive index oils using a 10X dispersion staining objective (central stop mode). The majority of light minerals are examined in 1.540 oil while micas and talc are examined in 1.585 oil. Enhanced differentiation was noted when Cargille Series E high dispersion oils (R.P. Cargille Laboratories Inc., Cedar Grove, NJ) were used for these lower indices. Amphibole and pyroxenes are examined in 1.660 and 1.690 oils which also permits the carbonates to be differentiated. Additional heavy minerals such as garnet and epidote are examined in 1.780 oil. Thirty or more minerals can be identified by this scheme and also compared to standard reference minerals, thereby allowing forensic soil examination to be performed by examiners with reasonable microscopic skills.

Although the method is by no means an exhaustive mineralogical workup of a soil sample, it does provide a substantial amount of data which can be extremely valuable for comparative purposes.

REFERENCES

Graves, W. J. (1978). A mineralogical soil classification technique for the forensic scientist, J. Foren. Sci. 24:323-337.

Kerr, P. F. (1977). Optical Mineralogy, 4th ed., McGraw-Hill, NY, 1959.

McCrone, W., Delly, and Palenik, S. (1979). The Particle Atlas, Vol. 5, No. 2, Ann Arbor Science Publishers Inc., Ann Arbor, MI, pp. 1158–1165.

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THE FORENSIC SIGNIFICANCE OF DIATOMACEOUS EARTH TRACE EVIDENCE IN WASHINGTON STATE

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Diatoms are photosynthetic, microscopic, unicellular algae ranging in size from less than 0.75 μm to more than 4000 μm secreting a test or skeleton of silica. Having a world-wide distribution, diatoms are found almost anywhere there is sunlight, moisture, and nutrients. In addition to living forms, fossil diatoms have formed large deposits by the slow accumulation of dead silicious cells on the floors of lakes and oceans. The earliest diatom forms have been documented from the Cretaceous Period, 63-73 million years ago.

During the Miocene period, approximately 12 m.y.o., flood basalts, today known as the Columbia River Basalt Group, extruded magma across much of present day Washington and Oregon. During periods of volcanic quiescence, lakes formed leaving lacustrine deposits, many of which contained thick beds of diatomaceous earth.

Two case studies are discussed demonstrating the usefulness of diatomaceous earth as trace evidence in Washington State.

Case one involved a suspected stolen truck tires recovered from the trunk of a vehicle in eastern Washington. Adhering to the tires was a small amount of brownish, powdery residue. Examination of the material by polarized light microscopy revealed pumice, limestone, basaltic rock fragments, organic debris and diatoms. Several tires from a local mining company's property were reported missing shortly before the recovery of the stolen tires. A diatomaceous earth control from the mining company was also submitted for examination. Examination of the control material revealed a freshwater diatom assemblage which included *Melosira, Coscinodiscus, Tetracyclus, Fragilaria, Navicula, Cymbella ?, Pinnularia ?, Eunotia ?*. A frequency distribution curve was prepared from both the suspect tires and the control. Both suspect and control materials contained a freshwater assemblage with a similar distribution of genera, suggesting they both could have a common origin.

Case two was a homicide which occurred in eastern Washington in 1987. The body of a known prostitute was discovered with gray granular material adhering to her hands, fingers and under her fingernails. Examination of the particles revealed plagioclase, quartz, phyllosilicates, basaltic rock fragments, and diatoms. The diatoms were of common fossil marine origin, including *Coscinodiscus, Actinoptychus, Thassionema nitzschioides Grunow, Thalassiothrix, Opephora, Rhabdonema, Synedra, and Cymatopleura ?*. The area where the body was discovered did not contain diatomaceous earth, although central Washington contains numerous lacustrine diatomaceous earth deposits. The presence of marine assemblage diatoms on the victim and the lack of marine diatomaceous earth deposits in central Washington presented a working hypothesis; diatomaceous earth found on the victim was from a local industrial or agricultural source, not a naturally occurring locality. In this arid, agricultural and wine producing region of Washington, the victim may have been in contact with diatomaceous earth used in swimming pool filters, winery filtration, or material used as a carrier for insecticides and fertilizer.

In conclusion, the taxonomic identification of individual diatoms, the uniqueness of their assemblage, and the determination of their depositional paleoenvironment may be used as strong associative evidence helping place suspects or evidentiary material at a crime scene.

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MORPHOLOGICAL EXAMINATION OF GRASS FRAGMENTS IN FORENSIC SOIL COMPARISON

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Soil has great potential value as evidence which links a suspect to a crime scene. A number of methods has been adopted for comparison of soil samples concerning their complexity. Major techniques generally used in forensic laboratories, however, were petrological ones. Although minerals are major component of soil, mineralogical methods such as optical examination of primary minerals and X-ray diffractometry (XRD) on clay minerals are not always applicable, because a soil distributes in the space along a landscape frequently having mineralogical homogeneity. In this case, it was necessary to examine parameters independent of geological materials, for example, enzymatic activity of soils or plant opals.

In this study, two techniques were applied to examination of small grass fragments in soils for forensic soil comparison.

MATERIALS AND METHOD

1 - Materials - 50 species of gramineous grass leaves were collected from the low altitude region in Japan.

2 - Surface view of leaf - A chip of dried leaf sample was boiled in water for 30 minutes and dipped in ethanol or acetone. The chip was cut into two pieces by a razor blade, then each piece was arranged on a carbon specimen mount side by side to enable us to observe both upper epidermis and lower epidermis on the same field of view. The samples were examined by scanning electron microscope under the magnification of 200 to 400.

3 - Viewing of plant opals - A chip of dried leaf sample was ashed in electric furnace under the controlled temperature from 100 up to 600°C, by 50°C every 30 minutes. Then ashed sample was sealed on a slide glass with Canada balsam carefully so as not to give a serious damage. The specimen was examined under a microscope using magnification of 100 to 200.

RESULTS

Lower epidermis system in the surface view showed characteristic structure according to each species as shown in Figure 1. Useful parameters for comparison were form and size of stoma, epidermis cells and papillae.

In the slide of ashed grass leaf, plant opals which showed forms of silicificated cells were clearly observed as shown in Figure 2. Form and orientation of plant opals were specific in grass species.

CONCLUSIONS

According to specificity of the structure of lower epidermis system and plant opals, examination of grass fragments offers good information to forensic soil comparison. If the photographs are prepared for references, grass species can be identified.

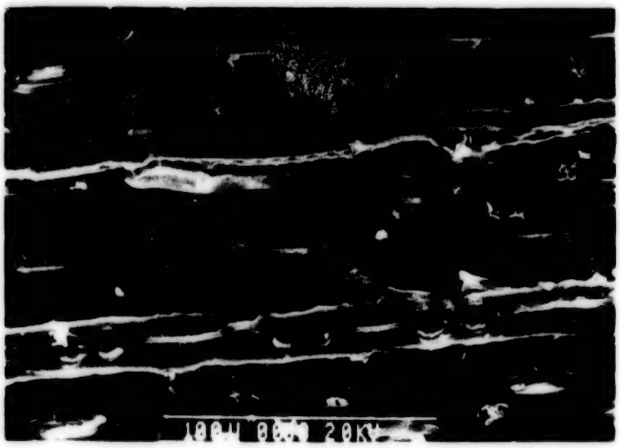

Figure 1. Surface view of lower epidermis system of Miscanthus sinensis.

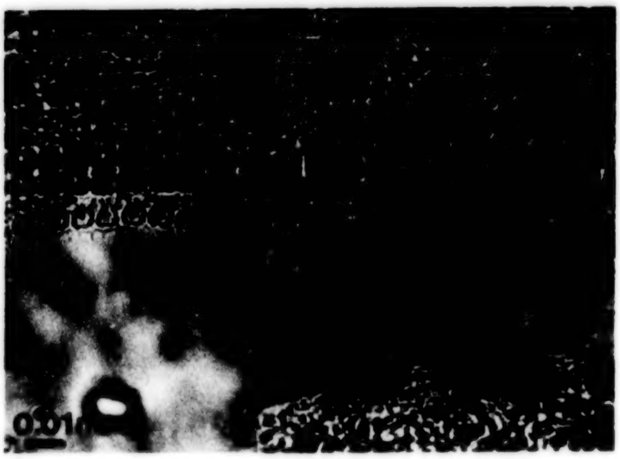

Figure 2. Plant opals in ashed leaf of Oryza sativa (rice plant).

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THREE-MAN SCREENING TECHNIQUE FOR TRACE EVIDENCE RECOVERY

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A recent excavation of a two car garage, with a partly dirt and partly concrete floor, led to an improvisation for the rapid examination of large quantities of dirt for the detection of trace evidence. Special agents of the FBI were led by an informer, at the end of October 1990, to a house with a separate back-yard garage. This was ostensibly the burial site of at least three former members or enemies of the Patriarca family, New England's dominant crime organization. A valid search warrant was obtained in order to attempt to determine if graves were indeed present at the site.

When the contents were removed from the wooden garage, side-by-side recent and remotely poured concrete floors were observed. These floors were separated by about 0.76 m of dirt which was connected to a sodden floor that extended the length of the back of the garage, forming a "T-shape". Using a long metal rod, the dirt areas were systematically probed and two locations were found to have extremely loose soil; these being the vertical and right limbs of the "T".

Two recovery teams of Connecticut State Police, FBI agents, and the medical examiner excavated the sites by standard hand techniques removing 32-36 cubic m of dirt next to the holes. As per procedure, a 0.76 m square sieve framed by 5 x 10 cm boards and finished with 0.64 cm screen was placed across two saw horses to begin sifting the excavated soil for evidence. No obvious large human remains were noted. The standard sifting process proved labor intensive and tedious.

Recovery team members proposed and subsequently devised a modification to increase sifting efficiency and reduce evidence recovery time. Two parallel long wooden handles were appended to sides of the sifter. Two operators then held the handles and a third placed shovels of dirt on to the screen. The operators then, in unison, rocked the sifter back and forth causing the loose dirt to rapidly filter away. Larger solids were then inspected by the operators for trace evidence. Using this technique, teams of three for each of the grave sites recovered valuable skeletal evidence including 78 [illegible] elements composed partly of two hyoid bones, [illegible] fourth metacarpals, indicating that at [illegible] distinct individuals had been buried there. [illegible] included fibers consistent with a sweater that [illegible] of persons was known to wear, human hair that was similar to one of the missing men, fragments of plastic bag and lime, and a .22 caliber shell casing. The larger debris composed of gravel, partial and complete animal remains, and other trash was retained for future review, if needed, in a large plastic garbage can.

Investigators believe that over a six year period, at least three individuals who were known to be associated with the mob and turned up missing, were surreptitiously killed and buried in the garage. Persons involved in the original burial became aware of the possibility of an impending operation and attempted to remove the boney remains. The axial skeleton, limbs, and skulls were obviously readily recovered and disposed of, but the small more cryptic bones and other trace evidence were left behind. Assisted by this spontaneously conceived modification, enough evidence was recovered to facilitate multiple arrests. One of the suspects, the owner of the garage, was known to mob associates as "the digger".

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A STRANGE CASE OF ANALYSES ON THE TESSERA OF AN ANCIENT MOSAIC

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We report an unusual case of analyses of some tessera belonging to a mosaic dating back to the early Christian period. It was stolen during a theft carried out in a palace of a noble family located in the center of Rome.

The purpose of this test was to establish, through comparative analytical investigations, whether a half-tessera, which was found within a bag belonging to the suspected thief, had characteristics similar to the ones of four tessera found at the basis of the wall on the floor of the apartment where the mosaic was located.

The first comparison was carried out using the stereoscopic microscope through which two very similar tessera were singled out among the four belonging to the original mosaic. Out of the two, one in particular was nearly identical to that found in the suspected thief's bag.

Two kinds of investigations were carried out:

- the analysis of the lodging mortar;
- the analysis of the glassy tessera;

In the first case the idea was to check the composition of the material used to stick the tessera to the wall. Glossy and thin cross-sections were obtained which were examined with the stereoscopic microscope under transmitted and reflected light. Both mortars showed the same structure and composition essentially made up of carbon lime, without any aggregates such as marble powder, siliceous sand or pozzolana.

In the second case, we wanted to verify the nature of the glass matrix used for the manufacturing of the tessera, establishing the exact qualitative and quantitative nature of the elements present in the glass, such as vetrifiers, fluxes, opacifiers, dyes, stabilizers, etc. Using a thin diamond blade small fragments were cut which were embedded in resin and the sections were polished. The samples obtained were examined by an X-Ray Microanalysis (Cameca SX-50), performing an average analysis based upon three tests for each sample. In this case too, both the crystalline and the glass phases showed a composition which could be perfectly overlapped. This, together with the same nature of the mortar, indicated the great likelihood that the tessera under investigation comes from the same mosaic and hence that the suspected was guilty of the theft.

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TRACE ELEMENT ANALYSIS
OF GLASS FRAGMENTS
BY ICP-AES WITH ULTRASONIC NEBULIZATION

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The FBI Laboratory currently utilizes inductively coupled plasma-atomic emission spectrometry (ICP-AES) to aid in discrimination of glass fragments. Sample size is a limiting factor, however, and it is necessary to have between two and five mg of the questioned glass. Because forensic samples frequently do not meet this weight requirement a modified method of analysis was sought. Ultrasonic nebulization was selected due to its desolvation capability and availability.

MATERIALS AND METHODS

Glass standard reference material (SRM) 1831 (National Institute of Standards and Technology, Gaithersburg, MD) was used for this study. The glass fragments to be analyzed were first washed in concentrated nitric acid and then rinsed with deionized water followed by ethanol. The fragments were dried in an 80°C oven and then cooled in a desiccator. The glass fragments were crushed between sheets of polyethylene to obtain desired sample weights. Samples were accurately weighed and placed in 15 ml polyethylene tubes.

To each sample tube was added 500 µl of Optima HF (Fisher Scientific, Pittsburgh, PA). The tubes were then placed in an 80°C oven for about one hour after which they were sonicated and returned to the oven and taken to dryness. After drying, 500 µl of concentrated Optima HCl (Fisher Scientific, Pittsburgh, PA) was added to each sample tube. Again, each was dried completely.

Finally, 500 µl concentrated HCl, 50 µl 1000 ppm PE Pure Scandium (Perkin-Elmer Corp., Norwalk, CT) and 9.45 ml deionized water were added to each sample and each tube was capped, vortex mixed, and returned to an 80°C oven for one hour. The samples were allowed to cool to room temperature and analyzed by ICP-AES using multi-element standards prepared from 1000 ppm PE Pure AA standards (Perkin-Elmer Corp., Norwalk, CT). Triplicate measurements were made on each solution and scandium was used as an internal standard for all elements quantified except sodium. ICP-AES and ultrasonic nebulizer parameters are given in Table 1.

RESULTS

Table 2 shows the results of nine separate samples of glass SRM 1831 analyzed using a high solid nebulizer and nine separate samples quantified utilizing an ultrasonic nebulizer. The certified values for SRM 1831 are also listed. Both sets of results fall within acceptable limits from the certified values. Some of the deviation that does exist, especially for elements like Sr, Ti, and

Table 1. INSTRUMENTAL AND ANALYTICAL CONDITIONS FOR ICP-AES

Instrumentation	
Spectrometer Model	Perkin-Elmer Plasma II
Dispersing System	Monochrometer A: 3600 grooves mm^{-1}, resolution $\leq$ 0.009 nm, 160-400 nm
	Monochrometer B: 1800 grooves mm^{-1}, resolution $\leq$ 0.018 nm, 160-800 nm
Torch	Fassel-type
Nebulizer	Perkin-Elmer high solids *or* Cetac Technologies U-5000
Spray Chamber	Scott design
Rf Generator	27.12 MHz, 1.2 kW forward power
Analytical conditions	
Argon flow rates	Plasma 15 L min^{-1}
	Auxiliary 1.0 L min^{-1}(High-solids neb.)
	Auxiliary 1.2 L min^{-1}(Ultrasonic neb.)
	Nebulizer 1.0 L min^{-1}
Sample uptake rate	High solids nebulizer 1.0 ml min^{-1}
	Ultrasonic nebulizer 2.0 ml min^{-1}
Observation height	15 mm above load coil
Spectral lines, nm	Fe 238.204, Mg 279.553, Ti 334.941, Ca 393.366, Al 396.152, Sr 407.771, Na 589.592
Background correction	Auto
Signal compensation	On, all except Na
Integration time	100 msec
Additional Ultrasonic Nebulizer Conditions	
Heater 140°C	
Condenser 0°C	
Nebulizer Output 5 amps	

Table 2. TRACE ELEMENT CONCENTRATIONS(μg/g) IN SRM 1831 GLASS. HIGH-SOLIDS (HS) AND ULTRASONIC (US) NEBULIZER RESULTS ARE BASED ON TRIPLICATE SCANS OF NINE SEPARATE SAMPLES.

Element	Certified	HS	US
Al	6400 ± 200	5970 ± 40	6250 ± 70
Fe	610 ± 40	606 ± 10	607 ± 40
Sr	not certified	88 ± 1	80 ± 3
Mg	21200 ± 400	20000 ± 200	23500 ± 200
Ti	110 ± 10	107 ± 4	91 ± 3
Na	98800 ± 700	98700 ± 600	99700 ± 2300
Ca	58600 ± 300	59400 ± 500	60600 ± 500

Ca analyzed using the ultrasonic nebulizer and Al analyzed using the high-solid nebulizer are attributed to the concentration of the solution lying at the low end of the calibration curve used for quantitation. Two values were eliminated from the ultrasonic nebulizer method results based upon the Q-test, one an iron concentration of 0.0805% and the other a titanium concentration of 0.0349%. Quite possibly these erroneous numbers were a result of contamination during glass preparation.

CONCLUSIONS

Clearly, small glass fragments can be compared with good precision using ICP-AES with ultrasonic nebulization. Better accuracy may be obtained for certain elements such as Sr, Ti, and Ca by using less concentrated standards for the calibration curve. Due to the contamination possibility of such small samples, it is imperative that replicate samples be analyzed.

THE USE OF PHYSICAL CHARACTERISTICS FOR THE COMPARISON AND DISCRIMINATION OF GLASS PARTICLES

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The evidential value of the physical characteristics of glass chips recovered in casework has been discussed in several publications in recent years. Features of value include surface flatness, determined with interference objectives, (Lock and Zoro 1983) and the presence of rouge pits (Sild 1987). A recent case demonstrated the value of an additional feature, not previously reported. Moreover, the relatively new high performance architectural glasses are now being encountered in routine case work, providing further possible points of comparison.

Intruders gained access to a school by breaking several panes of wired glass, and climbing through. Two comparison samples were received, both showing the rouge pits characteristic of polished glass, and containing embedded chrome plated iron wire. Several glass fragments were recovered from the clothing submitted from the suspects, including particles exhibiting rouge pits, and indistinguishable by refractive index and density from each of the two comparison samples. In addition, two fragments of glass, approximately 3 mm in maximum dimension, showed a groove suspected to be from contact with the embedded wire. Elemental mapping of the glass particles using SEM/EDX showed an enhanced concentration of chromium along the groove on one particle, and an enhanced concentration of iron along the groove of the other.

Tests with wired glass confirmed that a small percentage of broken particles show this characteristic groove. The refractive indices of the two grooved case work particles were measured. The particle with enhanced chromium matched one of the two comparison samples submitted, but as expected, the particle with enhanced iron differed from both.

The so-called high performance glasses are sheets of float glass which have been pyrolitically coated or sputter coated with thin layers of metals, metal oxides or metal nitrides to achieve architecturally desirable optical or thermal properties. Not surprisingly, these are now being encountered in routine case work. Where the coating is coloured, surface chips recovered from the clothing of a burglary suspect are immediately recognizable through the low power stereo binocular microscope. The elements in the surface coating are readily identifiable by SEM/EDX. However, the so-called low-E glass, which has improved thermal insulation properties, is effectively transparent. Pyrolytically coated low-E glass has a surface coating of tin oxide, sprayed on at the time of manufacture, while the glass is still in the float lehr. Sputter coated glass is made by a process, separate from the glass manufacture in which a thin coating of silver, sandwiched between layers of either tin oxide or zinc oxide is sputtered on to the surface under very low gas pressure from specially designed electrodes.

Samples of both pyrolytic and sputter coated low-E glass were obtained from AFG Glass of Concord, Ontario, and examined using SEM/EDX. Enhanced concentrations of silver and zinc were readily identified in the coated surface of the sample of sputter coated glass. However, for the pyrolytically coated glass, the concentration of tin in the coated (non-fluorescent) surface was similar to that found in the float surface of normal float glass. Sputter coated low-E glass encountered in case work should therefore be readily identifiable; however, work remains to be done in order to reliably identify the pyrolytically coated product.

REFERENCES

Lock and Zoro, (1983). The examination of glass particles using the interference objective. Part 1, Foren. Sci. Int., 22:221–231.

Sild, (1987). A surface feature specific to polished plate and polished wired plate glass, Can. Soc. Foren. Sci. J., 20:155–156.

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SYSTEMATIC APPROACH TO THE IDENTIFICATION OF EXPLOSIVE RESIDUES
VI. SLURRY/GEL AND EMULSION EXPLOSIVES

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The traditional commercial high explosive, dynamite, is being replaced by cap sensitive water gel/slurry or the newer emulsion explosives and this is reflected in evidence received in our laboratory. Advantages of these explosives over dynamite are cost, safety in production and handling, and ease of use.

Water gel explosives consist of an aqueous phase gelled with a cross linked polysaccharide, primarily guar gum. The oxidizer, ammonium nitrate alone or with other oxidizing salts, is in solution in the gel. Dispersion of additional oxidizer or solid fuel in the gel produces a slurry and most commercial water gel explosives are actually slurries.

In high energy slurries or emulsions, paint grade or atomized aluminum is added as fuel. Emulsions consist of two distinct phases, typically water in oil, with the oxidizer suspended as aqueous droplets in a hydrocarbon medium of wax, mineral or #2 fuel oil.

Blasting agents are not initiated by a #8 detonator but sensitizers can be added to these slurry or emulsion formulations to make them cap sensitive. Aluminum, amine nitrates and glass or plastic microspheres are widely used as sensitizers. Microspheres differ in composition, resemble tiny balloons and control density as well as providing sensitization. Patented chemical sensitizers in water gel/slurries, particularly amine nitrates, may permit compound identification to indicate product type or manufacturer. Sensitization of emulsions is frequently by microspheres alone.

Because the literature offers little guidance to the analysis and characterization of these types of high explosives, an analytical scheme of color tests, TLC, optical microscopy and GC for intact materials has been devised. For additional characterization, analytical methods include X-ray Diffraction (XRD), Scanning Electron Microscopy/Energy Dispersive X-ray (SEM/EDX), Ion Chromatography (IC), and HPLC with Thermal Energy Analysis (TEA) or GC/TEA. Initially, physical characteristics such as packaging, color, odor, and gel character are noted.

Water gel/slurry explosives are typically packaged in plastic sleeves twist-tied at the ends like sausages, from 2-10 cm diameter and 20-40 cm long. Emulsions tend to be dry rather than sticky and may be packaged in wax paper wrappers resembling sticks of dynamite.

Low power stereo-microscopy is used to identify microspheres, aluminum or other particulate materials. Spot tests include Nessler, modified Greiss, aniline sulfate and NaOH for NH_4^+, NO_3^-, ClO_3^- and Al respectively. Fuel oil or microcrystalline wax is identified by extraction into an organic solvent and analysis by GC. Ammonium or sodium nitrate and other oxidizers can be identified by IC and XRD and sensitizers, for example, methylamine nitrate (MMAN), monoethanolamine (MEAN), hexamine nitrate, ethylene glycol mononitrate (EGMN), etc., by TLC, IC, HPLC/TEA or GC/TEA (Parker 1975; Peterson *et al.* 1983; Prime and Krebs 1984).

The accompanying flow chart (Figure 1) encompasses all analytical approaches described. Although component identification should be confirmed by two distinct techniques, with intact, unexploded material, all the analytical approaches described need not be used. From the physical and analytical information developed and general formulation information, the type and producer of a water gel/slurry or emulsion explosive can be tentatively identified.

REFERENCES

Parker, R. G. (1975). Analysis of explosives and explosive residues. Part 3: Monomethylamine nitrate, J. Foren. Sci. 20:257–260.

Peterson, G. F., Dietz, W. R. and Stewart, L. E. (1983). Identification of explosives containing alkylammonium nitrates by thin-layer chromatography, J. Foren. Sci. 28:638–643.

Prime, R. J. and Krebs, J. (1984). The Analysis of Ethyleneglycolmononitrate and Monomethylamine Nitrate from Commercial Blasting Agents in Post Blast Samples, Can. Soc. Foren. Sci. J. 17:35–40.

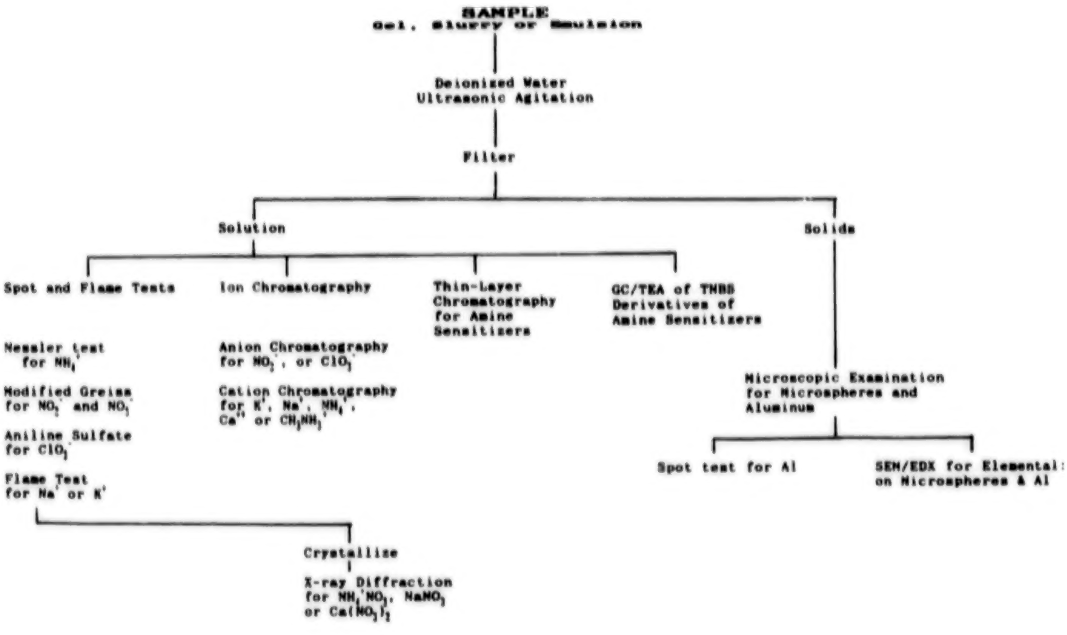
SAMPLE
Gel, Slurry or Emulsion
Deionized Water
Ultrasonic Agitation
Filter
Solution
Solids
Spot and Flame Tests
Ion Chromatography
Thin-Layer Chromatography for Amine Sensitizers
GC/TEA of TNBS Derivatives of Amine Sensitizers
Nessler test for NH_4^+
Modified Greiss for NO_2^- and NO_3^-
Aniline Sulfate for ClO_3^-
Flame Test for Na^+ or K^+
Anion Chromatography for NO_3^-, or ClO_3^-
Cation Chromatography for K^+, Na^+, NH_4^+, Ca^{++} or $CH_3NH_3^+$
Crystallize
X-ray Diffraction for $NH_4^+NO_3$, $NaNO_3$ or $Ca(NO_3)_2$
Microscopic Examination for Microspheres and Aluminum
Spot test for Al
SEM/EDX for Elemental: on Microspheres & Al

Figure 1. Flow chart for analytical approach for explosive residues.

A SIMPLE, INEXPENSIVE THERMAL DESORPTION METHOD FOR THE TRACE ANALYSIS OF HEADSPACE VAPORS FROM EXPLOSIVES AND ORGANIC NITRO COMPOUNDS

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The inexpensive headspace method described in this paper was developed to identify the trace vapor components in the headspace of explosives for the purpose of evaluating detectors of explosives vapors. Several manufacturers claim to have detectors that can detect low vapor pressure explosives such as the plastic explosive Semtex. It is imperative that the actual compounds to which these detectors respond are known, in case the detector does not respond to the primary high explosives.

MATERIALS AND METHODS

Headspace samples above explosives and nitro compounds were collected onto stainless steel Tenax traps with the aid of a small pump at a flow rate of 20 cc/min. Samples were thermally desorbed from these Tenax traps (Figure 1) via a Luer-lok fitting with a syringe needle, placed through a heating block and into the septum of a gas chromatograph (Figure 2). A narrow bore capillary column was used with a split injector with zero split flow and detection by electron capture, thermal energy analysis, or mass spectrometry if sufficient sample were trapped.

RESULTS

In this study, the headspace vapors above 120 explosives, propellants, and organic nitro compounds were analyzed in order to identify the trace components above explosives and determine retention times for compound identification. The results show that numerous explosives samples stored in commercial explosives magazines, become contaminated with traces of other explosives and can give misleading indications of response to the primary, low vapor pressure explosive. The concentration of these trace vapors cannot easily be quantitated. The levels are below the low pg level, since for many compounds, trace components were not observed when using gas chromatography-mass spectrometry even for trappings times as long as a few hours. However, for these same compounds, trace peaks were observed with the electron capture and thermal energy analyzers.

CONCLUSIONS

The simple inexpensive headspace method described in this paper would be appropriate for bomb scene investigations, gun shot residue analysis and arson debris analysis. For trace analysis, gas chromatography with either electron capture or thermal energy analysis would be the most sensitive method. Quantitation would be with known standards and compound identification by retention time matching.

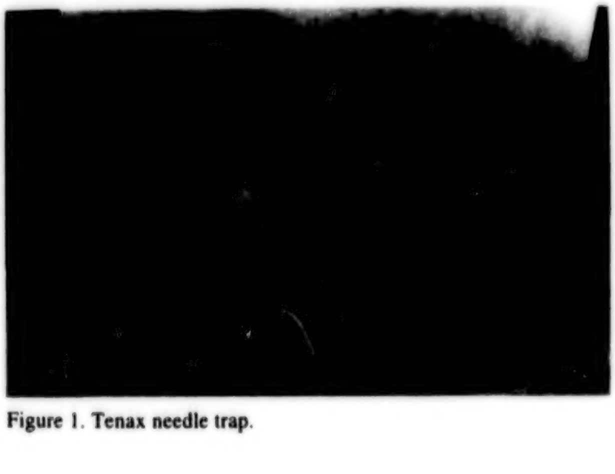

Figure 1. Tenax needle trap.

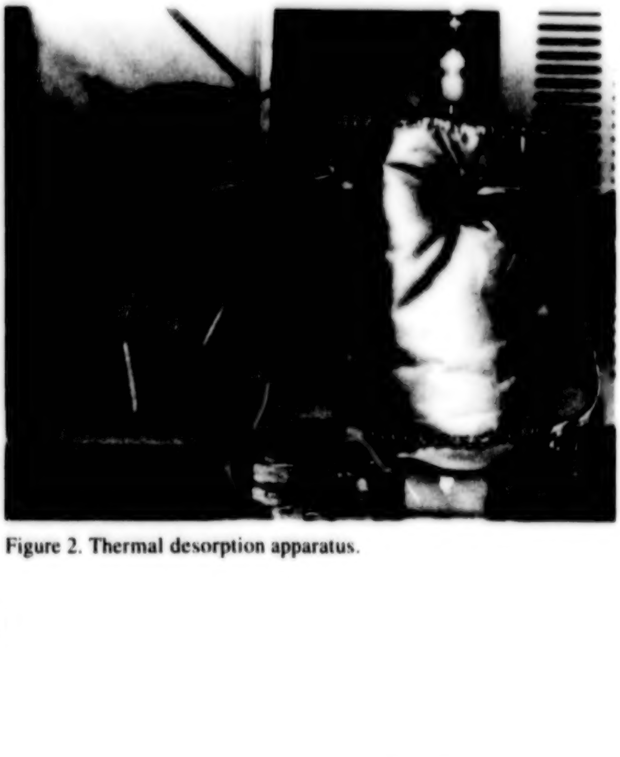

Figure 2. Thermal desorption apparatus.

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ULTRA-TRACE ANALYSIS OF EXPLOSIVES BY GAS CHROMATOGRAPHY WITH ELECTRON CAPTURE DETECTION: AN OPTIMIZATION STUDY

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We have previously performed studies on the use of gas chromatographs as a source of explosive vapors (vapor generator) and it was well known that adsorption is the major factor which limits working at pg levels of TNT and RDX. For these reasons an optimization study was taken to determine which parameters were responsible for adsorption and how these can be minimized.

Factors studied included the time for splitless injection, priming of the injection port, the type and the nature of deactivation of injection liners, and the injection port temperature. Studies involved the analysis of replicate injections of 40 pg of RDX in 2-propanol. Both peak areas and peak symmetries were measured. These results were then treated by analysis of variance and conclusions drawn.

Times for splitless injection studied were 15, 30 and 45 seconds. At each time three replicate injections were made. Table 1 shows the results. As the f value of 1.39 for data set did not exceed the critical value of 5.143, there was no significant difference among the different splitless times at the 95% confidence level. As a result we chose to use 15 seconds as this minimizes the possibility of thermal decomposition.

The second parameter tested was priming the injection port. Priming was accomplished by slowly injecting 80 g of RDX in 2 ml of 2-propanol over a period of 30 seconds. This saturated the injection port with RDX vapor which would hopefully temporarily cover any active adsorption sites. After the priming injection, a temperature ramp was initiated to clean the RDX from the column. Following the temperature ramp, a blank run was performed to ensure that the GC was clean. The results show that there is a very significant difference in the area counts due to priming. The probability that any difference is due to random variation is 0.004, which means that the difference is significant at the 99.6% confidence level.

Table 1. DATA FROM SPLITLESS TIME STUDY.

Splitless Time sec	Area Counts
15 sec	933
15 sec	826
15 sec	906
30 sec	850
30 sec	760
30 sec	813
45 sec	773
45 sec	919
45 sec	789

The fact that priming increases peak area significantly indicates that there are active sites in the chromatographic system. While an established GC procedure, (certainly for packed columns) priming is merely a temporary band-aid, not the solution to the adsorption problem.

For each set of data, peak area, height and area to height ratio were used in separate analyses of variance. The data show that there is a very high probability of a difference due to liner configuration (99.99% confidence level).

The results clearly show that the Restek 2 mm gooseneck liner in an unprimed state was the most inert in terms of both peak area and height. This liner showed the least irreversible adsorption and was used in all future studies.

The last parameter tested was the injection port temperature. Temperatures ranging from 160°C to 240°C at intervals of 20°C were used to analyze in triplicate a solution of 39.5 pg/μof RDX in 2-propanol. The results from these analyses show that the highest area resulted from an injection temperature of 220°C. Table 2 shows the parameters changed as a result of these studies

Using these optimized conditions the chromatogram shown in Figure 1 was obtained. This level is about two orders of magnitude below any other literature values indicating the need for a very clean GC system.

Table 2. CHANGES IN PARAMETERS AS A RESULT OF OPTIMIZATION.

Parameter	Old Conditions	New Conditions
Splitless time	30 sec.	15 sec.
Priming of Injector	none	none
Splitless Liner	HP Commercial	Restek 2 mm GN
Injection Temperature	200°C	220°C

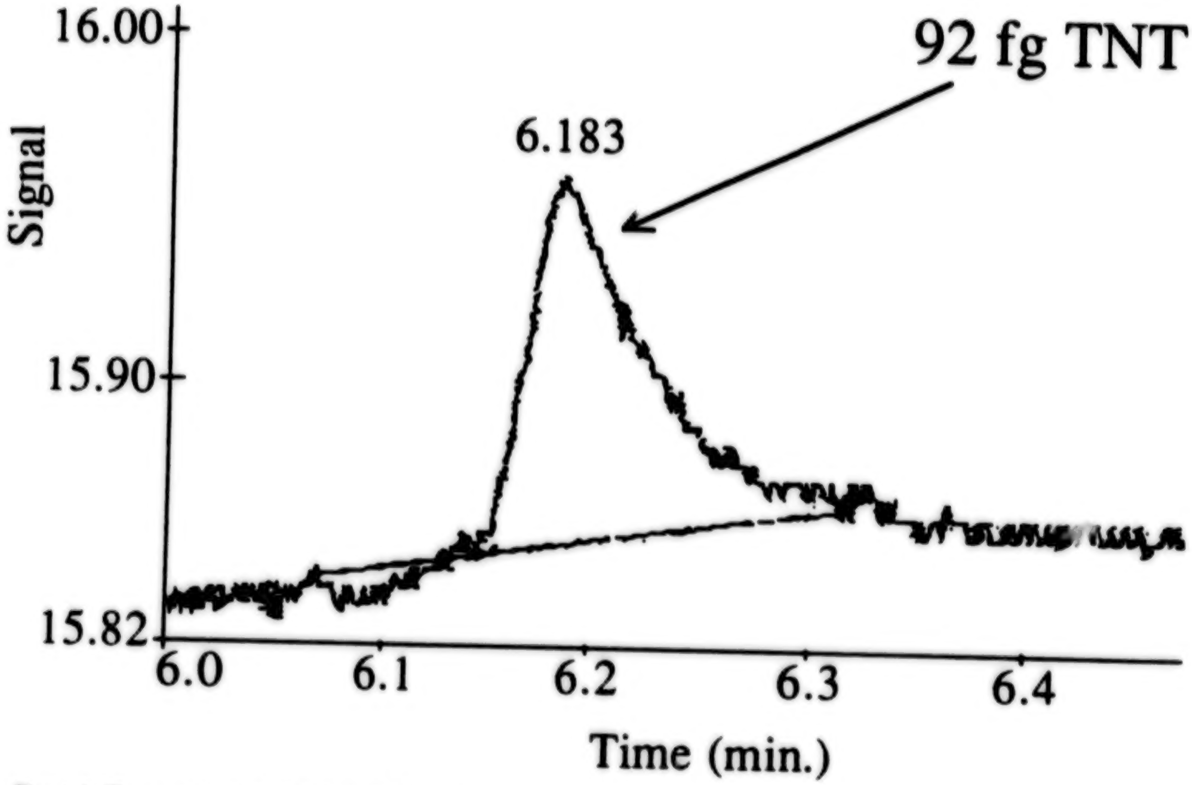

Figure 1. Chromatogram of 90 fg/µTNT by ECD.

ANALYSIS OF PLASTIC BONDED EXPLOSIVES I: AN ANALYTICAL SCHEME FOR THE SEPARATION AND CHARACTERIZATION OF COMPONENTS

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Plastic bonded explosives (PBXs) represent a serious threat because of their availability to many terrorist organizations and ease of concealment. Trace components incorporated in the manufacture of these materials can provide unique characteristics which individualize the explosive material. This type of information can help the investigator identify the source of the PBX and aid in determining the network of supply in the terrorist community.

An analytical scheme for the systematic separation and identification of the components present in many types of PBXs has been developed. An ordered series of solvent extractions sequentially isolates the binders, explosives, oils, plasticizers, and dyes. In this scheme, a 50 mg portion of the PBX sample is first subjected to an acetone extraction which isolates the insoluble binder. The dried extract, containing explosives and additives, is weighed, and the additive package, which consists of various oils, plasticizers, and dyes, is extracted with hexane. Solid phase extraction is then performed on the hexane extract by injecting it into a SEP-PAK silica cartridge (Waters, Milford, MA). This step is used to isolate the oils from the other additives. The plasticizers and dyes are next desorbed from the cartridge with methylene chloride.

After weighing each fraction, the components are identified and characterized by a variety of analytical techniques including high-performance liquid chromatography (HPLC), gas chromatography (GC), gas chromatography/mass spectrometry (GC/MS), Fourier transform infrared spectrometry (FT-IR), and gel permeation chromatography (GPC). The molecular weight distribution of the polymeric binders is determined by GPC prior to the extraction. The binders are then identified by FT-IR following isolation by the acetone extraction.

The explosive fraction is analyzed by HPLC with diode array detection and confirmed by FT-IR. HPLC provides quantitative information on the relative amounts of explosives in the explosive fraction, and diode array detection allows the peaks to be identified by their UV spectra. Oils are characterized by high-temperature GC, while plasticizers and dyes are separated and examined by GC/MS.

Semtex, an explosive of Czechoslovakian manufacture, is a good example of the materials that are analyzed by this method. This PBX contains the high explosives RDX and PETN in a poly(styrene: butadiene) binder. Using the previously described procedure, specific information on the quantity and types of additives in the bulk material has been obtained. Variations have been found in the molecular weight and relative monomer content of the binder, in the impurities in the explosive fraction, and in the oils and dyes in the additive package. The combined results of these analyses yield a unique signature which provides source information as well as links between incidents in which PBXs are found.

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EXPLOSIVE RESIDUE ANALYSIS BY CAPILLARY ELECTROPHORESIS AND ION CHROMATOGRAPHY

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In the blast of a low explosive, a complex series of chemical reactions takes place with catastrophic results. The goal of the forensic chemist is to piece together clues from the residue left behind which can point to the type of the explosive material used. For many years, the most powerful tool in these investigations has been ion chromatography. Using this technique, ppm levels of the anions and cations left behind from the blast are easily seen and quantitated. Unfortunately, ion chromatographic analysis suffers from the lack of a good complementary technique for peak confirmation, but the recent development of capillary electrophoresis (CE) for ion analysis has provided an opportunity to improve this situation. While still producing information in a format very similar to ion chromatography, the CE system operates using a completely different separation mechanism. The combination of these two techniques results in a nearly orthogonal separation that is an ideal complementary technique.

For the CE analysis method, a pH 7.8 buffer system consisting of 40 mM borate with 1.8 mM dichromate and a 1 mM diethylenetriamine electro-osmotic flow modifier has been selected (Dionex 1991). In this method the polarity is set to produce flow towards the positive electrode, and sample ions are detected by monitoring the loss in absorbance at 265 nm as they pass through the detector cell. Electro-osmotic flow inside the capillary moves the buffer and analyte ions towards the detector, and separation occurs as a result of differences in electromigration of the anions.

The ion chromatographic method uses indirect photometric detection at 280 nm. A Vydac 302IC (Vydac, Hesperia, CA) column with a 1.5 mM isopthalic acid eluent at pH 4.6 is used with a pump flow rate is set to 2.0 ml/min (Bender 1989). The procedure has been used routinely in this laboratory for more than two years, and is capable of separating all of the major anions present in low explosive residues.

Experimental work focused on comparing results taken with the IC and CE systems. A variety of solutions of ion standards were prepared and analyzed using both CE and IC. Elution order and retention times were drastically different. Peaks for the CE system were sharp with high theoretical plate counts, but poor separation limited the dynamic range of the technique. The IC system achieved superior separations for certain peaks, but was less efficient and required a longer analysis time.

To examine forensic applications of the combined techniques, a series of explosive devices were prepared and ignited. Analysis of the aqueous extracts of the residues was performed on both systems. Peak assignments were facilitated by overlaying chromatograms from both the IC and CE systems and comparing retention times (Figure 1). The large differences in separation mode and order between the two techniques simplified the analysis of the results, clarifying ambiguous assignments.

REFERENCES

Bender, E. (1989). Indirect photometric detection of anions for the analysis of low explosives. Crime Lab. Digest 16:78–83.

Dionex (1991). Application Note #68.

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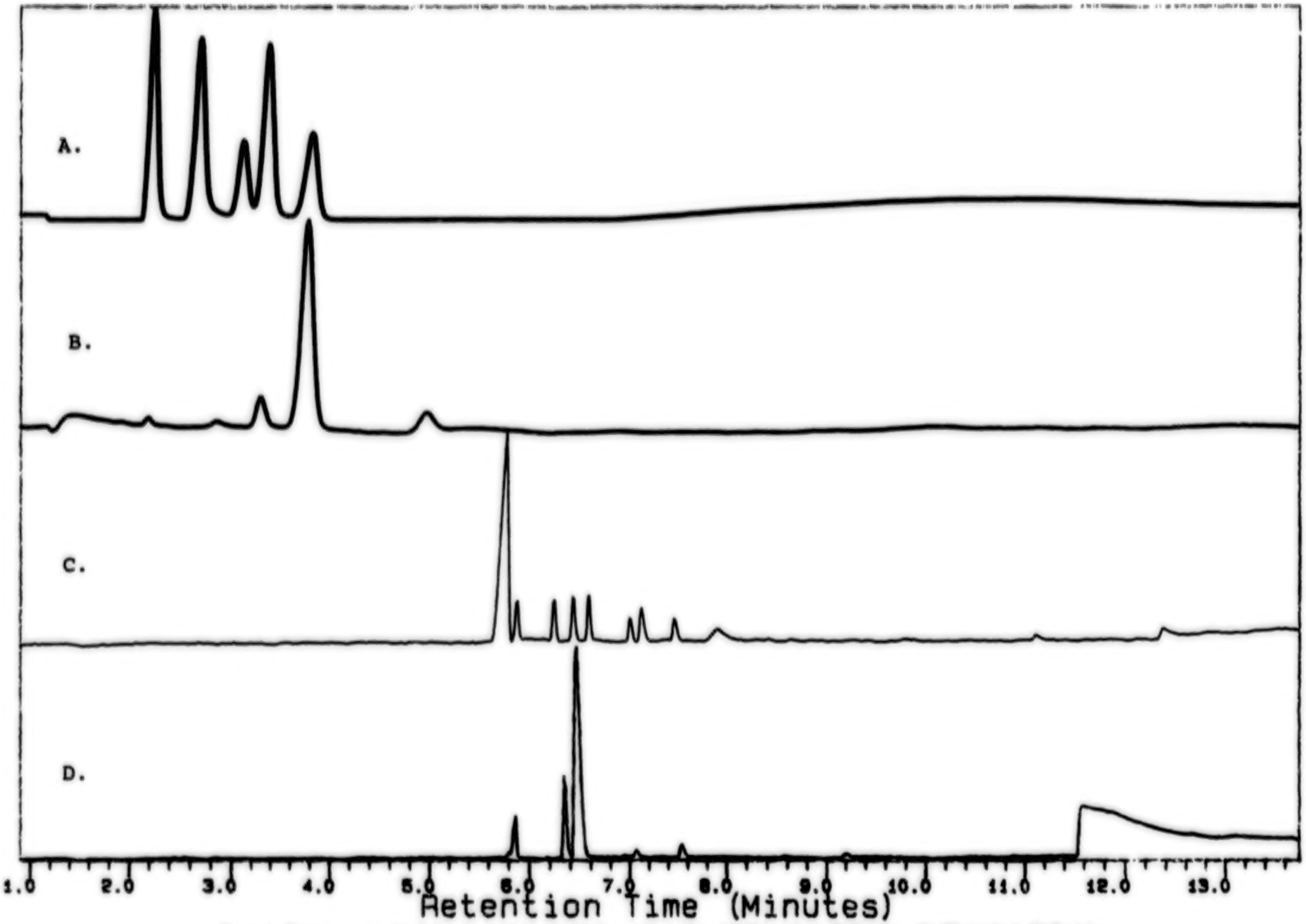

Figure 1. Chromatograms displaying the analysis of a black powder residue: (A) IC standard, (B) Residue, (C) CE standard, (D) Residue. Peak order for IC standard: Cl, NO_2, ClO_3, NO_3, and SO_4. Peak order for CE standard: Br, Cl, NO_2, NO_3, SO_4, ClO_4, SCN and ClO_3.

ANALYSIS OF PLASTIC BONDED EXPLOSIVES II: BULK ANALYSIS BY INFRARED INTERNAL REFLECTION SPECTROSCOPY

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Plastic bonded explosive (PBX) formulations are frequently very complex and analysis of these materials by bulk infrared (IR) spectrometry is not commonly performed. Sample preparation difficulties and problems with spectral interpretation has limited the application of this method. A solution to the preparation problem is internal reflection spectroscopy (IRS). This technique, also known as attenuated total reflection (ATR), easily overcomes sample mounting difficulties and is nondestructive. Milligram samples can be conveniently pressed against the internal reflection crystal to obtain good contact and can readily be removed for additional analysis. Additionally, the current availability of digital spectral libraries and computerized searching capabilities makes possible the rapid screening of plastic explosive materials.

An IR data base was created from IRS spectra acquired of PBX's characterized by the methods outlined by Tungol *et al.* (1993). Searching these reference spectra provided assistance in determining the source of the explosive and helped to link explosives found in different incidents. Major components were often identified by searching a specialized explosive component library.

EXPERIMENTAL

Samples weighing 200-300 mg were matted against a 45° KRS-5 internal reflection crystal on a Model 300 accessory produced by Spectra-Tech, Inc. (Stamford, CT). The spectrometer was an Nicolet (Madison, WI) 20SXC FT-IR with a broad band MCT detector. The spectrometer was operated at 4 cm^{-1} resolution, with a range of 4000-450 cm^{-1} and scanned 128 times. The data base was produced from approximately 50 commercial samples of known composition and previously analyzed case samples. Individual components were used to establish a small explosive components library. The components of this additional library were sampled by diffuse reflectance and KBr pellets.

RESULTS AND DISCUSSION

The ability to search the libraries was tested by resampling known plastic explosives. Figure 1 shows the spectrum of a questioned sample compared to the first hit on the library search for PBX's. As can be observed by the spectra, the composition is very close to C-4, a U. S. military explosive. The second hit was the same sample which was run one year previous to this run. This library search provided a good screening of the PBX sample, rapidly determining the explosive type. Subsequent analysis by liquid chromatography revealed the absence of HMX which is present in U. S. made C-4, thus indicating a foreign made explosive.

RDX, the known major component of C-4, was the first library selection for the component search of the sample. Figure 2 shows that all the peaks in the RDX spectrum are in the mix. Additionally, the mixture spectrum has bands from the other components.

CONCLUSION

The application of infrared internal reflection spectroscopy with subsequent computer searching of reference libraries has been very valuable in the screening of plastic bonded explosives.

REFERENCES

Tungol, M. W., Whitehurst, F. W., Keagy, R. L. and McCord, B. R. (1993). Analysis of plastic bonded explosives I: An analytical scheme for the separation and characterization of components, In: Proceedings of the International Symposium on the Forensic Aspects of Trace Evidence, U. S. Government Printing Office, Washington, D. C., pp.

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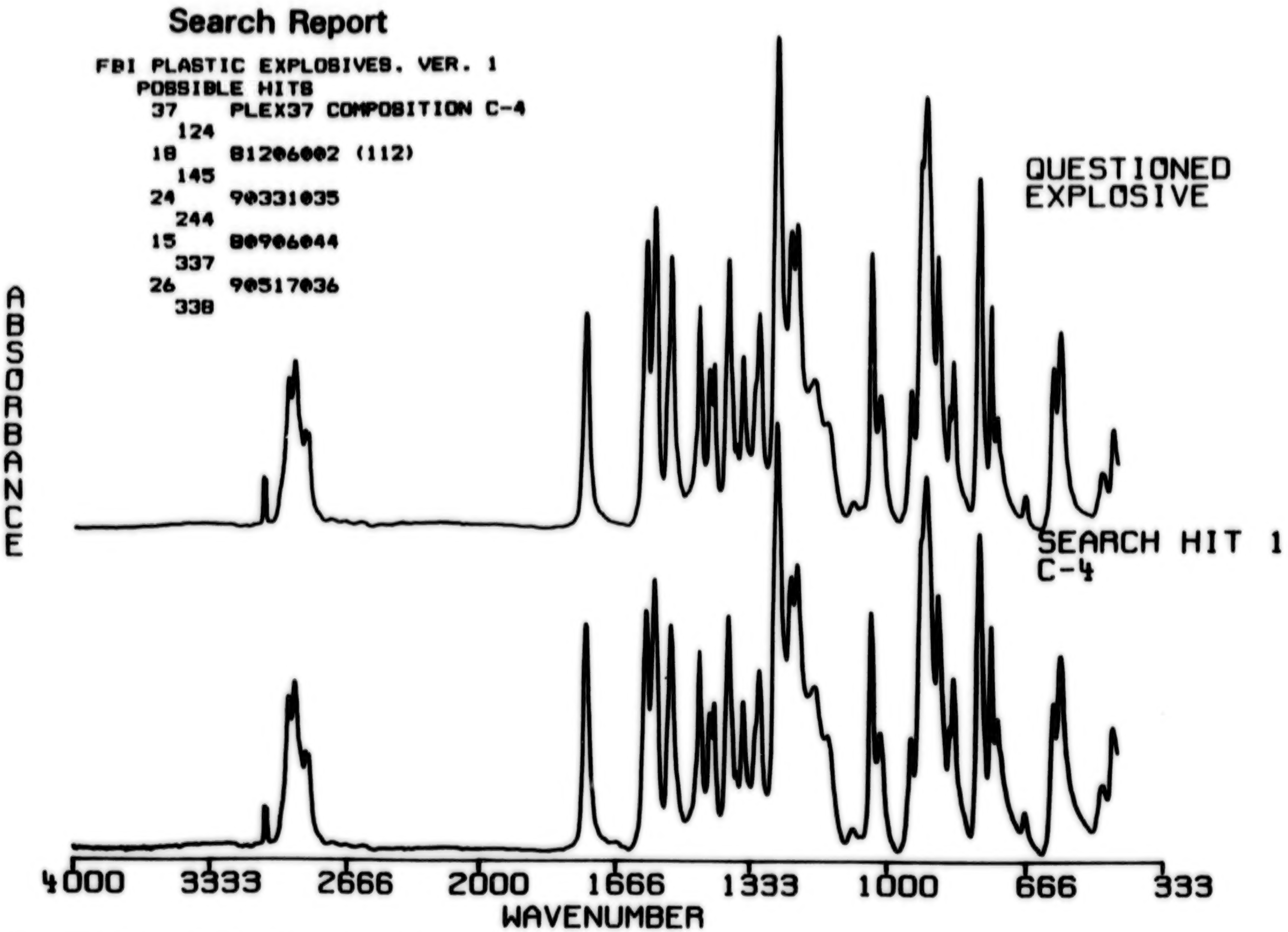

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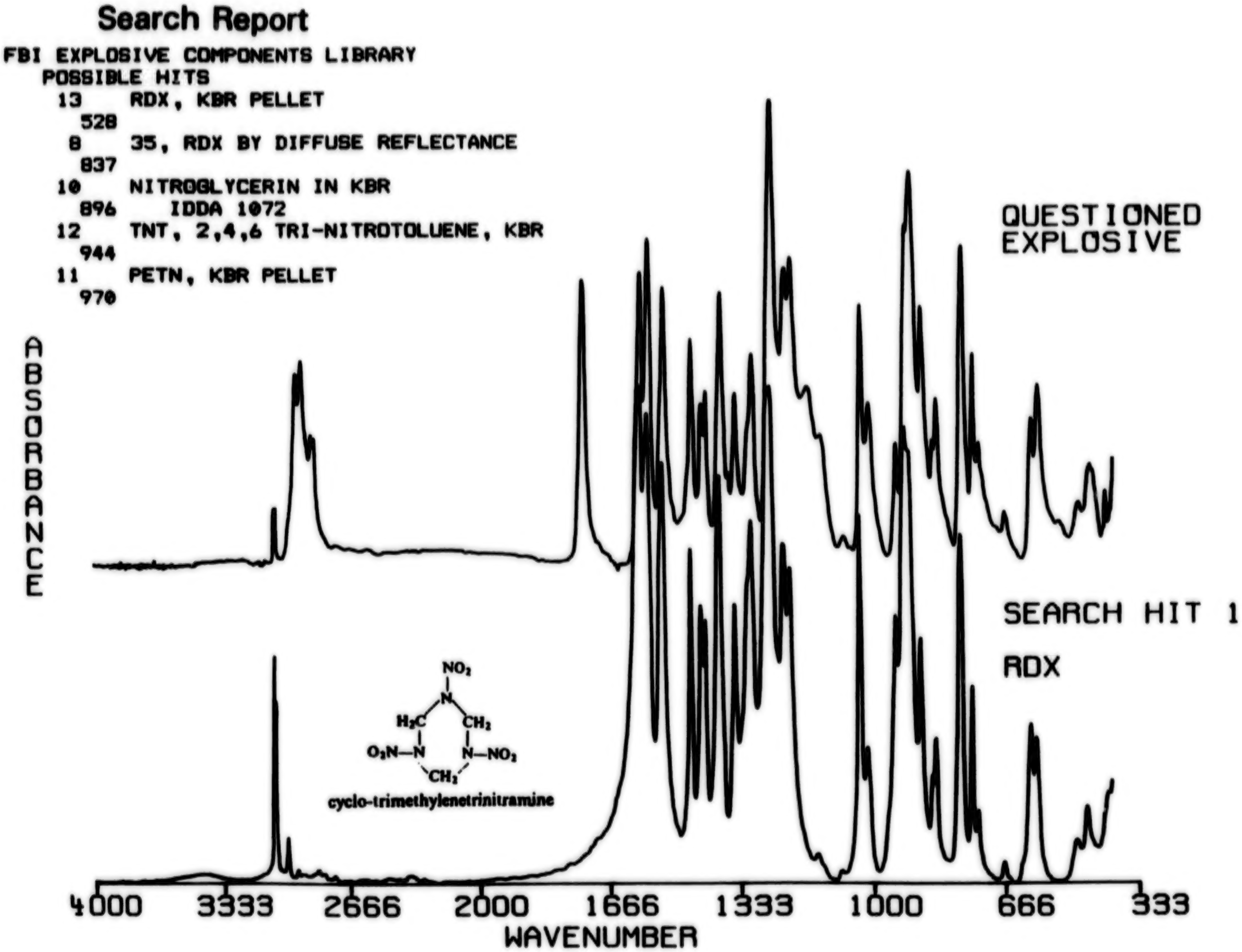
Search Report

FBI PLASTIC EXPLOSIVES. VER. 1
   POSSIBLE HITS
    37     PLEX37 COMPOSITION C-4
      124
    18     81206002 (112)
      145
    24     90331035
      244
    15     80906044
      337
    26     90517036
      338
```

Figure 1. Search results for questioned plastic explosive searched against the general PBX library.



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Search Report
FBI EXPLOSIVE COMPONENTS LIBRARY
   POSSIBLE HITS
    13    RDX, KBR PELLET
     528
     8    35, RDX BY DIFFUSE REFLECTANCE
     837
    10    NITROGLYCERIN IN KBR
     896     IDDA 1072
    12    TNT, 2,4,6 TRI-NITROTOLUENE, KBR
     944
    11    PETN, KBR PELLET
     970
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Figure 2. Search results for questioned plastic explosive searched against the explosive components library.

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